Issued June 29, 1907.

U. S. DEPARTMENT OF AGRICULTURE.

BUREAU OF CHEMISTRY—BULLETIN No. 105.

H. W. WILEY, Chief of Bureau.

PROCEEDINGS

OF THE

TWENTY-THIRD ANNUAL CONVENTION

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS,

HELD AT

WASHINGTON, D. C., NOVEMBER 14–16, 1906.

EDITED BY

HARVEY W. WILEY,

SECRETARY OF THE ASSOCIATION.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Chemistry,
Washington, D. C., February 28, 1907.

Sir: I have the honor to transmit for your approval the proceedings of the Twenty-third Annual Convention of the Association of Official Agricultural Chemists. The growth in the work of the association has made it imperative that both papers and discussion be condensed as far as possible, and all methods or other material which can be found in other generally available sources are given only by reference. I recommend that this report be published as Bulletin No. 105 of the Bureau of Chemistry.

Respectfully,

H. W. Wiley,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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FIRST DAY.

WEDNESDAY—MORNING SESSION.

The twenty-third annual convention of the Association of Official Agricultural Chemists was called to order by the president, Mr. C. G. Hopkins, of Urbana, Ill., at 10 o'clock on the morning of November 17, at the George Washington University, Washington, D. C.

The following members and visitors registered during the convention:

MEMBERS AND VISITORS PRESENT.

Adams, Arthur B., Bureau of Internal Revenue, U. S. Treasury Department, Washington, D. C.

Albrech, Maximilian C., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

Allen, William M., Department of Agriculture, Raleigh, N. C.

Alwood, William B., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

Ames, John W., Agricultural Experiment Station, Wooster, Ohio.

Arnold, Robert B., Box 726, Richmond, Va.

Bartlett, James M., Agricultural Experiment Station, Orono, Me.

Beal, W. H., Office of Experiment Stations, U. S. Department of Agriculture, Washington, D. C.

Bell, James M., Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

Bigelow, W. D., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

Bishop, Harry E., Indiana Laboratory of Hygiene, Indianapolis, Ind.

Bizzell, James A., Agricultural Experiment Station, Ithaca, N. Y.

Blair, A. W., Agricultural Experiment Station, Lake City, Fla.

Bowker, W. H., Bowker Fertilizer Co., Boston, Mass.

Brinton, Clement S., Food Laboratory, U. S. Department of Agriculture, Philadelphia, Pa.

Browne, Charles A., jr., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

Burnet, Wallace C., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

Burton, Joseph Q., Atlanta, Ga.

Cameron, Frank K., Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

Carpenter, F. B., Virginia-Carolina Chemical Company, Richmond, Va.
Carroll, John S., German Kali Works, Atlanta, Ga.
Chace, Ed. MacKay, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Chamberlin, Joseph S., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Church, C. G., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Cochran, Carlos B., Department of Agriculture, Westchester, Pa.
Cook, Frank C., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Crampton, Charles A., Bureau of Internal Revenue, U. S. Treasury Department, Washington, D. C.

Davidson, Robert J., Agricultural Experiment Station, Blacksburg, Va.
Donk, Marion G., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Doolittle, Roscoe E., Food Laboratory, U. S. Department of Agriculture, New York, N. Y.
Dox, Arthur W., Agricultural Experiment Station, Storrs, Conn.
Doyle, Aida M., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Dubois, Wilbur L., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

Ellett, Walter B., Agricultural Experiment Station, Blacksburg, Va.
Frear, William F., State College, Pa.
Frost, Howard V., Food Laboratory, U. S. Department of Agriculture, Chicago, Ill.
Fuller, F. D., Department of Agriculture, Harrisburg, Pa.

Gamble, Wm. P., Ontario Agricultural College, Guelph, Canada.
Gascoyne, Wm. J., 2741 North Charles street, Baltimore, Md.
Given, Arthur, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Gooden, Edward H., Bureau of Internal Revenue, U. S. Treasury Department, Washington, D. C.
Goodrich, Charles E., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Gore, H. C., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Goss, Willard L., Bureau of Plant Industry, U. S. Department of Agriculture, Washington, D. C.
Gould, Ralph A., Food Laboratory, College of Agriculture, Berkeley, Cal.
Graham, J. J. T., Agricultural Experiment Station, College Park, Md.
Gray, C. Earl, Bureau of Animal Industry, U. S. Department of Agriculture, Washington, D. C.

Hand, William F., Agricultural Experiment Station, Agricultural College, Miss.
Hanson, Herman H., Agricultnral Experiment Station, Orono, Me.
Hardin, Mark B., Agricultural Experiment Station, Clemson College, S. C.
Hargrove, Julian O., 1603 O street, Washington, D. C.
Harris, C. D., Assistant State Chemist, Raleigh, N. C.
Harrison, Channing W., Food Laboratory, U. S. Department of Agriculture, New Orleans, La.
Hart, Benj. R., Agricultural Experiment Station, Lexington, Ky.
Hartwell, Burt L., Agricultural Experiment Station, Kingston, R. I.
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Hill, D. H., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Hite, B. H., Agricultural Experiment Station, Morgantown, W. Va.
Holland, Ed. B., Hatch Experiment Station, Amherst, Mass.
Holland, Herbert J., Food Laboratory, College of Agriculture, Berkeley, Cal.
Hoover, Geo. B., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Hopkins, Cyril G., Agricultural Experiment Station, Urbana, Ill.
Horne, Wm. D., National Sugar Refining Company, Yonkers, N. Y.
Houghton, Harry W., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D C.
Howard, Burton J., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Howard, Charles D., Board of Health, Concord, N. H.

Jones, Charles H., Agricultural Experiment Station, Burlington, Vt.
Jones, Wm. J., jr., Agricultural Experiment Station, Lafayette, Ind.

Kebler, Lyman F., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
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Leavitt, Sherman, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Le Clerc, J. A., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Lind, Herman, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Langworthy, C. F., Office of Experiment Stations, U. S. Department of Agriculture, Washington, D. C.
Lythgoe, Herman C., State Board of Health, Boston, Mass.

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McDonnell, Henry B., Agricultural Experiment Station, College Park, Md.
McGill, Anthony, Chemist to Canadian Government, Ottawa, Canada.
Magruder, E. W., Department of Agriculture, Richmond, Va.
Mason, Glen F., H. J. Heinz Company, Pittsburg, Pa.
Mathis, Walter R., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Mewborne, Robert G., Kentucky Tobacco Product Company, Louisville, Ky.
Mooers, Charles A., Agricultural Experiment Station, Knoxville, Tenn.
Moore, C. C., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Morgan, Jerome J., Agricultural Experiment Station, College Park, Md.
Munson, L. S., The Ault Wibourg Co., Cincinnati, O.

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Peter, Alfred M., Agricultural Experiment Station, Lexington, Ky.
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Reed, Howard S., Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.
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Robinson, Floyd W., State Analyst, Lansing, Mich.
Ross, B. B., State Chemist, Auburn, Ala.
Runyan, Elmer G., Inspector of Gas and Meters, Washington, D. C.

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Schreiner, Oswald, Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.
Schulz, Henry L., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Seidell, Atherton, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Sherwood, Sidney Forsythe, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
'Sigmond, Alexius A. J. de, University of Budapest, Hungary.
Sindall, Harry E., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
Skinner, W. W., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.
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Street, John Phillips, Agricultural Experiment Station, New Brunswick, N. J.
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Winton, A. L., Agricultural Experiment Station, New Haven, Conn.
Woll, Fritz W., Agricultural Experiment Station, Madison, Wis.
Woods, Charles D., Agricultural Experiment Station, Orono, Me.

Young, Wm. J., Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

FOOD ADULTERATION.

No general report on food adulteration was submitted and the reports of the associate referees were received in the following order:

REPORT ON COLORS.

By E. F. Ladd, *Associate Referee.*

In view of the fact that there is little definite knowledge with regard to color reactions, and especially as to the behavior of natural colors with reagents, it seemed desirable this year that some special attention be given to this phase of the work. Unfortunately this investigation must be conducted in laboratories already overcrowded with other lines of work, and several of the chemists cooperating have been unable to carry their experiments far enough to make a definite report. The present paper, therefore, may be said to be only a preliminary report on the work undertaken.

The investigation has consisted largely of individual work on special phases rather than cooperative work on samples sent out. But two reports have been received—one dealing with solubility and extraction of colors and the other with the detection of certain commercial colors designated as vegetable colors and used in food products. The reports expected on colors containing tin, antimony, etc., and on the testing of certain colors not readily extracted from an acid solution by means of amyl alcohol, are not yet ready for presentation.

At times it is with difficulty that the coloring matter is extracted from preserved fruits by means of amyl alcohol. It has been suggested (Pharmaceutisch Weekblad) that the use of ethyl alcohol and amyl alcohol in equal volumes as the extracting medium will prove more satisfactory than the use of amyl alcohol alone. The test is made as follows: Five grams of material are rubbed up with 5 cc of water and this warmed with 20 grams of ethyl and methyl alcohol in concentrated form. After cooling, additional water is added and if foreign coloring matters are present the same

will be contained in the layer of alcohol, which readily separates from the rest of the mixture. Not enough work has been done to test the value of this method of extraction.

RECOMMENDATIONS.

I repeat the suggestions of the associate referee for 1905, namely, that the members of the association and collaborators interested in the subject of colors do what original work their time will permit on the points suggested below:

(1) Solubility of the coal-tar and vegetable dyes in various solvents (ether, acetic ether, petroleum ether, methyl and ethyl alcohols, acetone, etc.), arranged according to their solubility—as, easily soluble, difficultly soluble, and insoluble.

(2) Extractive values of the various solvents for dyes in neutral, acid, and alkaline solutions.

(3) Characteristics of the coloring matters as contained in fresh fruits, vegetables, wines, etc., with reagents and solvents, and their respective dyeing properties.

(4) Testing such new schemes as may appear in the various current chemical journals, and such as have appeared during the last few years.

EXPERIMENTAL WORK ON COLORING MATTERS.

By H. M. LOOMIS.

The subreport on colors by Mr. H. M. Loomis, chemist, Pennsylvania Department of Agriculture, is published as Circular No. 35 of the Bureau of Chemistry, being too lengthy for publication in the Proceedings. This report includes four tables on the following subjects: Solubilities of colors; extraction of colors; color reaction on dyed fibers, and reactions of colors in aqueous solution and with concentrated sulphuric acid.

The subreport on colors by Mr. Nickles follows:

THE DETECTION OF CERTAIN COMMERCIAL COLORS ALLEGED TO BE VEGETABLE COLORS.

By A. G. NICKLES.

The investigation of colors during the past year in the laboratory of the North Dakota Agricultural College consisted in an effort to find some general method by which the commercial colors alleged to be vegetable dyes which are used in foods and beverages on the market to-day can be distinguished from colors of coal-tar origin. A line of such commercial colors from two of the leading manufacturing firms was used as a basis for the work. The plan of the investigation included the extraction of colors from their solution by immiscible solvents, the fixing of colors on wool, double dyeing method, and color reactions in aqueous solutions with certain reagents.

The accompanying table shows that thirteen of the fourteen colors examined gave a reaction for coal-tar dye, according to the double dyeing method of Sostegni and Carpentieri. Many of these alleged vegetable dyes which have been sent in for examination during the year have been found to give a similar permanency of color. In testing such of these dyes as color wool in the second dyeing, make careful note of the following points:

Use as little of the dye as possible; if the color is taken up readily in the first bath, notice carefully the reactions as the wool is boiled in the second acid bath. In nearly

every instance, if the color is of the class under consideration the solution will become more or less colored, while if the color is a coal-tar dye the solution will remain perfectly clear. There is a lack of brilliancy in all the alleged vegetable colors that dye wool, while on the other hand this feature is well marked in the coal-tar colors.

Since complete reliance can not be placed on the use of the Sostegni and Carpentieri method for the identification of coal tar colors, we were led to investigate the following method:

Extract the colors by the use of solvents such as ether, amyl alcohol, acetic ether, and acetone from solutions both in alkaline and acid condition. Evaporate the combined extracts separately to dryness in the presence of a piece of wool, and then make tests on the dyed fiber. Comprehensive tables of color and their reactions will enable the analyst to classify, if not identify, the color by the use of this method.

Most vegetable dyes give specific color reactions with ammonia. This fact has prompted quite a thorough investigation of the differentiation of the alleged vegetable colors from those of coal tar origin. The writer has observed the following reactions in working with the former class of commercial colors:

Place about 100 cc of water in a beaker of 150 cc capacity, add just enough of the dye to color the solution, avoiding too deep a color. Next add ammonia water (sp. gr. 0.90) in excess, from 30 to 40 cc, stir well, and allow to remain 12 or 14 hours and note changes. Some colors, however, change more rapidly than others. Blue colors become colorless. Of the red colors some will change to a much deeper tinge, while in the case of cudbear the color is changed to violet. The green, yellow, orange, and brown colors are changed to different shades of amber. With the coal-tar dyes there is a permanency of color not met with in the alleged vegetable dyes. There are, however, some coal-tar dyes that give a color reaction with ammonia, but by making the solution acid the original color is restored.

In the examination of a color by the use of the Sostegni and Carpentieri double dyeing method and then carefully observing the color reactions with ammonia, the analyst can quite easily distinguish between coal tar and the alleged vegetable colors. The following table summarizes the results obtained:

Reaction of commercial colors, said to be of vegetable origin, with different reagents.

Commercial color.	Character of dyestuff.	Ether extract from—		Amyl alcohol extract from—	
		Acid solution.	Ammoniacal solution.	Acid solution.	Ammoniacal solution.
Carmine red	Powder	Colorless	Colorless	Red	Colorless.
Cladonol red	do	do	do	do	Do.
Vegetable red	do	do	do	do	Do.
Do	Paste	do	do	do	Do.
Vegetable violet	do	do	do	Blue	Do.
Vegetable yellow	do	do	do	Yellow	Do.
Do	Powder	do	do	do	Do.
Vegetable orange	Paste	Orange	Orange	Orange	Orange
Vegetable green	do	Colorless	Colorless	Light green	Colorless.
Do	Powder	do	do	do	Do.
Lazulem blue	Paste	do	do	Colorless	Do.
Vegetable blue	do	do	do	do	Do.
Do	Powder	do	do	do	Do.
Vegetable brown	Paste	do	do	Brown	Do.

Reaction of commercial colors, said to be of vegetable origin, etc.—Continued.

Commercial color.	Character of dyestuff.	Acetic ether extract from—		Reaction with ammonium hydroxid in aqueous solution after standing 14 hours.	Remarks.
		Acid solution.	Ammoniacal solution.		
Carmine red	Powder	Slightly colored.	Colorless	Dark red	Does not dye wool in second dyeing (Sostegni & Carpentieri method).
Cladonol red	do	Red	do	Violet	Colors wool in second dyeing.
Vegetable red	do	do	do	do	Do.
Do	Paste	do	do	do	Do.
Vegetable violet	do	Colorless	Yellow	Pinkish	Do.
Vegetable yellow	do	do	Colorless	Amber	Do.
Do	Powder	do	do	do	Do.
Vegetable orange	Paste	Orange	Deep orange	Very light amber	Do.
Vegetable green	do	Colorless	Colorless	Amber	Do.
Do	Powder	do	do	do	Do.
Lazulem blue	Paste	do	do	Becomes colorless	Do.
Vegetable blue	do	do	do	do	Do.
Do	Powder	do	do	do	Do.
Vegetable brown	Paste	Brown	do	Dark amber	Do.

REPORT ON SACCHARINE PRODUCTS.

C. H. Jones, *Associate Referee.*

The work of the referee on saccharine products has been confined to maple sugar and sirup, and particular attention has been given to malic acid value. The method sent out this year was slightly modified from that reported at the last meeting of this association.[a] Such changes as were made, however, were based on data obtained by Mr. Julius Hortvet and the writer, who conducted careful tests to locate if possible the cause of the variation in results reported in 1905.

Mr. Hortvet's correction applies to the method of washing the precipitated calcium malate. Instead of attempting to "wash until free from soluble calcium salt," the washing should cease when there is practical freedom from chlorids. The following figures furnished by Mr. Hortvet illustrate this:

Table 1.—*Effect of washing on malic acid value (Hortvet).*

[Precipitated calcium malate in alcohol, washed with hot 75 per cent alcohol.]

No.	Filtrate and washings.	0.50 per cent malic acid solution in sirup.	Vermont sirup.	Ohio sirup.
	cc			
1	[a] 200	.....	0.34	.....
2	[b] 125	0.43	.38	.....
3	[b] 105	.....	.51	.....
4	100	.47	.38	0.54
5	96	.....	.62	.59
6	94	.....	.69	.61

[a] Nearly. [b] Approximately.

No. 1. Washed until practically no reaction for calcium. It appears that calcium malate is slightly soluble in the hot 75 per cent alcohol.

No. 2. Washed beyond the point at which silver nitrate ceased to give a precipitate insoluble in nitric acid. There was, however, a precipitate with silver nitrate soluble in nitric acid. Slight reaction for calcium.

[a] U. S. Dept. Agr., Bureau of Chemistry, Cir. 23, 1905.

No. 3. Slightly beyond the point at which silver nitrate gave a precipitate insoluble in nitric acid.

No. 4. Precipitate with silver nitrate showed only faint milkiness when treated with strong nitric acid.

Nos. 5 and 6. More chlorids shown in last drops of filtrate than in No. 4.

Your referee, after conducting a series of tests on the reagents called for in the determination of malic acid value, concluded that the amount of ammonia added to make the solution "slightly alkaline[g]" was a disturbing factor, and quite largely responsible for some variations and many of the high results previously reported. It was learned from correspondence with different chemists familiar with the test that from a drop to one or more cubic centimeters of ammonia had been used.

TABLE 2.—*Test on reagents used for obtaining malic acid value (Jones).*

No.	Calcium chlorid.	Water.	Ammonia.	Alcohol.	Malic acid value.
	cc	cc		cc	
1	1	15	1 drop.	60	0.14
2	1	15	2 drops.	60	.26
3	1	15	0.5 cc.	60	.51
4	1	15	1 cc.	60	.78
5	2	15	0.5 cc.	60	.57
6	1	15	0	60	.00
7	1	15	0	60	.015
8	1	15	0	60	.02

The malic acid value figure is seen to vary directly with the excess of ammonia present, due to the precipitation of lime after heating and standing overnight.

Three samples were prepared for cooperative work. No. 1 was a sugar containing 60 per cent cane and 40 per cent maple sugar, No. 2 contained 60 per cent of light brown sugar [a] and 40 per cent of maple, while No. 3 was pure maple sugar. All of the samples were sugared off at 238° F.

Eighteen sets of samples were sent to chemists who had requested the same, together with the following methods of analysis and a letter of transmittal:

METHODS OF ANALYSIS.

Preparation of sample.

Just previous to analysis, pulverize or shave each cake, mix, and transfer to small, wide-mouth stoppered bottles.

Ash.

Weigh 5 grams of sugar into a tared platinum dish; heat over asbestos board until the contents are thoroughly carbonized; transfer to a muffle and burn at low red heat to a white or grey ash. Cool in a desiccator and weigh quickly. Dissolve the residue in about 40 cc of hot water and boil gently for two minutes, using care to avoid spattering. Filter through a small ashless filter and wash with hot water until the filtrate amounts to about 100 cc. Transfer filter and contents to the original platinum dish and incinerate at low red heat as before. Cool and weigh. Cool and titrate the solution containing the soluble ash with tenth-normal hydrochloric acid, using methyl orange as indicator. Add to the insoluble ash an excess of the tenth-normal acid (10 cc is usually sufficient) and about 30 cc of water. Boil gently until solution is complete. Cool and titrate with tenth-normal sodium hydroxid, using methyl orange as indicator. Calculate from the results obtained the percents of total ash, water soluble ash, insoluble ash, and the alkalinity of the soluble and insoluble ash, expressed as cubic centimeters of tenth-normal hydrochloric acid for ash of 1 gram of sample.

[a] Analysis: Ash, 0.53 per cent; soluble ash, 0.47 per cent; insoluble ash, 0.06 per cent; alkalinity, soluble ash, 0.50 cc; alkalinity, insoluble ash, 0.10 cc; malic acid value, 0.02 per cent.

Malic acid value.

Weigh $6\frac{7}{10}$ grams of the sample into a 200 cc beaker and add water to make a volume of 20 cc. Add 1 cc of a 10 per cent solution of calcium chlorid and heat to boiling. Now add 60 cc of 95 per cent alcohol, cover the beaker with a watch glass and heat for one-half hour on a water bath. Remove and let stand over night. Filter (through a 9 cm No. 589 S. & S. filter) by decantation. Transfer precipitate to the filter by washing with hot 75 per cent alcohol and continue the washing until entire filtrate measures 100 cc. Dry and ignite. Add from 15 to 20 cc of tenth-normal hydrochloric acid to the ignited residue, dissolve by careful boiling, cool and titrate the excess of acid with tenth-normal sodium hydroxid, using methyl orange as indicator. One-tenth of the number of cubic centimeters of acid neutralized expresses the result.

Report results as follows:

1. Total ash, per cent.
2. Soluble ash, per cent.
3. Insoluble ash, per cent.
4. Alkalinity of soluble ash, as cubic centimeters required for 1 gram of material.
5. Alkalinity of insoluble ash, as cubic centimeters required for 1 gram of material.
6. Malic acid value.
7. Comments and suggestions.

Thirteen analysts, representing twelve laboratories, have furnished results shown in the following table:

TABLE 3.—*Results of cooperative maple sugar work.*

No. 1.—ADULTERATED. 60 PER CENT CANE, 40 PER CENT MAPLE.

Analyst.	Total ash.	Soluble. ash.	Insoluble ash.	Alkalinity of soluble ash.	Alkalinity of insoluble ash.	Malic acid value.
	Per cent.	*Per cent.*	*Per cent.*	*cc.*	*cc.*	
A. T. Charron, Ottawa, Canada	0.29	0.15	0.14	0.29	0.43	0.10
E. B. Holland, Amherst, Mass	.30	.22	.08	.29	.34	.....
C. P. Moat, Burlington, Vt	.32	.20	.12	.30	.26	.06
M. C. Albrech, Washington, D. C	.30	.22	.08	.12	.22	.13
	.33	.28	.05	.12	.24	.12
E. Monroe Bailey, New Haven, Conn	.38	.26	.12	.20	.30	.03
	.37	.25	.12	.19	.28	.03
W. B. Pope, Concord, N. H	.33	.19	.14	.26	.40	.08
A. P. Sy, Buffalo, N. Y	.35	.26	.09	.30	.32	.03
C. H. Jones, Burlington, Vt	.32	.20	.12	.30	.28	.11
A. G. Nickles, Agricultural College, N.Dak	.29	.18	.11	a.18	a.20	a.01
A. Valin, Ottawa, Canada	.33	.23	.10	.24	.25	.09
	.35	.23	.12	.26	.26	.10
J. A. Miller, Buffalo, N. Y	.31	.20	.11	.29	.40	.08
R. M. West, St. Paul, Minn	.36	.21	.15	.21	.43	.09
F. T. Shutt, Ottawa, Canada	.25	.....	.....	.....	.....	.....
Average	.33	.22	.11	.24	.31	.08

No. 2.—ADULTERATED. 60 PER CENT LIGHT BROWN, 40 PER CENT MAPLE.

A. T. Charron, Ottawa, Canada	0.59	0.47	0.12	0.48	0.34	.07
E. B. Holland, Amherst, Mass	.47	.39	.08	.52	.38	.....
C. P. Moat, Burlington, Vt	.58	.43	.51	.51	.33	.06
M. C. Albrech, Washington, D. C	.47	.31	.16	.18	.34	.11
	.47	.32	.15	.16	.34	.11
E. Monroe Bailey, New Haven, Conn	.68	.52	.16	.34	.38	.04
	.67	.51	.16	.32	.38	.04
W. B. Pope, Concord, N. H	.59	.43	.16	.48	.58	.13
A. P. Sy, Buffalo, N. Y	.56	.45	.11	.53	.38	.05
C. H. Jones, Burlington, Vt	.57	.41	.16	.52	.31	.12
A.G.Nickles, Agricultural College, N.Dak	b.31	.23	.08	a.37	a.34	a.01
A. Valin, Ottawa, Canada	.52	.38	.14	.42	.34	.08
	.50	.36	.14	.44	.34	.07
J. A. Miller, Buffalo, N. Y	.51	.39	.12	.41	.48	.08
R. M. West, St. Paul, Minn	.58	.45	.13	.23	.40	.08
F. T. Shutt, Ottawa, Canada	.60	.....	.....	.....	.....	.....
Average	.56	.42	.14	.41	.38	.08

TABLE 3.—*Results of cooperative maple sugar work*—Continued.

No. 3.—PURE MAPLE SUGAR.

Analyst.	Total ash.	Soluble ash.	Insoluble ash.	Alkalinity of soluble ash.	Alkalinity of insoluble ash.	Malic acid value.
	Per cent.	*Per cent.*	*Per cent.*	*cc.*	*cc.*	
A. T. Charron, Ottawa, Canada	0.71	0.43	0.28	0.66	0.74	0.64
E. B. Holland, Amherst, Mass	.73	.44	.29	.60	.75	.....
C. P. Moat, Burlington, Vt	.72	.40	.32	.53	.64	.42
M. C. Albrech, Washington, D. C.	.82	.58	.24	.36	.70	.44
	.83	.59	.24	.44	.70	.47
E. Monroe, Bailey, New Haven, Conn.	.78	.44	.34	.53	.75	.23
	.78	.44	.34	.55	.74	.25
W. B. Pope, Concord, N. H	.75	.41	.34	.58	.88	.33
A. P. Sy, Buffalo, N. Y	.74	.46	.28	.60	.60	.29
C. H. Jones, Burlington, Vt	.78	.50	.28	.64	.64	.55
A.G. Nickles, Agricultural College, N.Dak.	.71	.49	.22	[a].48	[a].54	[a].16
A. Valin, Ottawa, Canada	.61	.34	.27	.42	.60	.50
	.62	.32	.30	.44	.64	.56
J. A. Miller, Buffalo, N. Y	.86	.58	.28	.64	.82	.22
R. M. West, St. Paul, Minn	.70	.39	.31	.41	.76	.41
F. T. Shutt, Ottawa, Canada	.74	.....	.....	.....	.....	.....
Average	.73	.44	.29	.53	.70	.39

[a] Phenolphthalein used as indicator. [b] Not included in average.

COMMENTS BY ANALYSTS.

A. T. Charron: The alcohol at my disposal did not contain 95 per cent absolute alcohol, and I believe my figures on malic acid value are low. Quite a difference in the appearance of ash was noticed. The ash of No. 3, besides being leafy and fluffy, contained manganese. All results are the mean of agreeing duplicates.

J. A Miller: Concerning malic acid value, would say that after washing until the entire filtrate measured 100 cc an additional washing with 75 per cent alcohol showed the presence of soluble lime salts in the filtrate. Adding 5 or 6 drops ammonia to 100 cc of filtrate, heating one-half hour on bath, and standing overnight, a further precipitate was obtained giving a malic acid value as follows: No. 1, 0.54; No. 2, 0.39; No. 3, 0.43.

A. P. Sy: Characteristic green color absent in above samples. For more accurate results would suggest that 10 grams be used for incineration.

M. C. Albrech: In addition to the work asked for by the referee the following data were supplied: Moisture at 70° C. in vacuum, No. 1, 5.12 per cent; No. 2, 6.73 per cent; No. 3, 7.73 per cent.

A. Valin: To establish uniformity of standards I would recommend that all results be stated for 100 grams of dry sugar. I also recommend that 35 per cent and 10 per cent moisture be adopted for sirup and sugar respectively, so as to permit the use of factors in calculation. The method for lead subacetate precipitate used in the Inland Revenue Laboratory is as follows: Five grams sugar or sirup are weighed into a test tube and dissolved in 20 cc of water. Two cc of lead subacetate solution (sp. gr. 1.26) are added and the solution mixed. After standing a few hours the mixture is filtered into a sugar tube, washed with warm water four or five times, dried, and weighed. The precipitate obtained, multiplied by 30.77 for a sirup and 22.22 for a sugar, gives the lead subacetate precipitate for 100 grams of dry sugar, assuming the sirup to contain 35 per cent and the sugar 10 per cent of water.

W. B. Pope: The method for malic acid value as outlined gives lower results than when ammonia is used. Length of time in boiling would also seem to be an important factor in securing comparable results, as it is evident that, unless the ash is finely divided, solution on heating is not quite so rapid a process as might possibly be inferred. Using the method for malic acid value outlined on page 321 of the Eighteenth Annual

Report of the Vermont Experiment Station, in which the solution is made slightly alkaline with ammonia, the following results were obtained: No. 2, 0.65; No. 3, 0.85.

E. M. Bailey: You will note that one determination of malic acid value in No. 3, using 0.5 cc of ammonia, gave a result of 0.77. This is much higher than the others, thus corroborating your experience. The difference between sucrose and total solids is considerably greater in No. 3 than in the others. We find that in samples of maple products, consisting largely of cane sugar, this difference is very slight indeed.

TABLE 4.—*Additional data on referee's samples determined by Bailey.*

Determinations.	Sample 1.	Sample 2.	Sample 3.
Total solids (per cent)	94.12	92.20	89.36
Sucrose (per cent)	89.70	86.46	81.05
Lead number	0.66	1.37	2.00
	.63	1.35	2.05
	.56	1.31	2.09
			2.13
Malic acid value, using 0.5 cc ammonia			.77

COMMENTS BY REFEREE.

With but few exceptions the results on the ash work are very satisfactory, and in all cases give data sufficient for the judging of purity. The figures showing alkalinity of the soluble and insoluble ash vary more than is desired. The reason for this, particularly in the case of soluble ash, is not clear.

The malic acid values again show surprising variations. It is worthy of note, however, that if the individual results by the different analysts are compared they show, without exception, the desired distinction between the pure and the adulterated samples. Taken in connection with the ash figures they show strikingly the sophistication of Nos. 1 and 2.

The conclusions of your referee as to the effect of ammonia on malic acid value are also confirmed by the additional data supplied by Messrs. Miller, Pope, and Bailey. (See comments by analysts.)

Attention was called last year to the special method of boiling and filtering and its use in detecting relatively small amounts of cane sugar added to maple goods.[a] The following results were obtained by its use on the association samples:

TABLE 5.—*Results obtained using special method of boiling and filtering.*

Determinations.	C. P. Moat.			C. H. Jones.		
	1.	2.	3.	1.	2.	3.
Total ash (per cent)	0.24	0.41	0.50	0.21	0.44	0.52
Soluble ash (per cent)	.14	.27	.27	.13	.30	.32
Insoluble ash (per cent)	.10	.14	.23	.08	.14	.20
Alkalinity soluble ash (per cent)	.20	.31	.39	.26	.39	.44
Alkalinity insoluble ash (per cent)	.24	.26	.45	.18	.31	.40
Malic acid value	.02	.04	.23	.08	.07	.33

Among other methods, useful in detecting the sophistication of maple goods, which should receive the attention of this association are the following:

(1) The determination of lead number devised by A. L. Winton.[b] This consists in determining indirectly the amount of lead in the precipitate formed in maple products by basic lead acetate. The method is easy of application and not very lengthy, particularly if sucrose is also to be estimated polariscopically. In this way it

[a] Eighteenth Annual Report of the Vermont Agricultural Experiment Station, 1905, p. 328.

[b] J. Amer. Chem. Soc., 1906, *28:* 1204.

is thought that the varying results from the two centrifugal methods in common use[a] can be stated on a constant gravimetric basis.

(2) Albert P. Sy has devised a method of determining lead directly in the lead acetate precipitate.[b] As briefly outlined in a letter to the referee it is as follows: Dissolve 25 grams of sirup or sugar in 300 cc of water, boil, add 20 cc of neutral lead acetate, let settle; filter, wash with 200 cc of water at 75° C., digest with aqua regia, add sulphuric acid, heat to fumes, cool, dilute, add alcohol, settle; filter, ignite, and weigh as lead sulphate. Calculate to 100 grams of material. The lead sulphate figures on the association samples by this method were as follows: No. 1, 0.0704; No. 2, 0.0684; No. 3, 0.288.

(3) Method of Hill and Mosher.[c] This method consists in removing the lead from the lead acetate precipitate by hydrogen sulphid, filtering, boiling, and titrating filtrate with tenth-normal alkali.

Recommendations.

The referee makes no formal recommendations, but suggests that if the work on maple products is continued that the three methods just mentioned be thoroughly tried. Also that consideration of the malic acid value be continued until a modification giving less variation among different operators is secured.

REPORT ON FRUIT PRODUCTS.

By Hermann C. Lythgoe, *Associate Referee.*

The following methods for the examination of lime juice, compiled by the referee, are in the main very satisfactory:

Specific gravity.—Make the determination of specific gravity in the usual manner.

Acidity.—Titrate 7 grams (6.8 cc if the gravity is about 1.04–1.05) with tenth-normal sodium hydroxid, using phenolphthalein as indicator. If the sample is colored, dilute with water. The burette reading divided by 10 gives the per cent of citric acid.

Solids.—Evaporate 5 grams of the sample in a flat-bottomed platinum dish for 2 hours over a boiling water bath, cool, and weigh.

Ash and soluble ash.—Make the determinations of ash and soluble ash on the residue obtained above as directed in Bulletin 65, p. 55. Examine for colors and antiseptics as usual—the antiseptics to be suspected are salicylic, benzoic, and sulphurous acids, and mixtures of these substances.

The determination of the alkalinity of the ash is given by several methods in the reports of this association, all of which give different results. This is a very valuable figure in the study of all fruit and vegetable products and there should be more uniformity in the methods. The method preferred by the referee is as follows:

Alkalinity of ash.—Evaporate 50 or 100 grams of the sample to dryness and prepare the soluble ash as described above. Add an excess of tenth-normal sulphuric acid, boil to expel the carbon dioxid, and titrate back with tenth-normal sodium hydroxid, using phenolphthalein as the indicator. Express results as cubic centimeters of tenth-normal acid required to neutralize the soluble ash of 100 grams of sample.

It is recommended that this association take some action to obtain greater uniformity in the determination of the alkalinity of the ash.

Mr. Bigelow. The determination of the alkalinity of the ash is very important in the work on fruit products, and two points especially should be considered and a uniform procedure established. The first one is to decide whether hot or cold water shall be used, and the second and more important point is to determine what indicator

[a] J. Amer. Chem. Soc., 1904, *26:* 1532; also Vermont Exper. Stat. Rpt. No. 17, 1904, p. 454.

[b] J. Franklin Inst., July, 1906, p. 71.

[c] Technology Quarterly, June, 1905, *18* (2): 147.

shall be employed. At present methyl orange is used for some products, phenolphthalein for others, and litmus in the case of determining tartaric acid compounds in wine by the titration of the ash. Because of this condition we have great difficulty in understanding published results and comparing the figures. Although Mr. Davidson as chairman of the committee on unification of terms for reporting analytical results has tried to get an expression of the opinion of the members of the association on this subject, only a very few of the members interested in the examination of foods have replied. As this committee and the committee on the revision of methods are preparing reports, it seems very important that the matter should receive the attention of the association.

REPORT ON BEER.

By H. E. Barnard.

The report of Mr. Barnard, Indiana State board of health, on methods of beer analysis is published as Circular No. 33 of the Bureau of Chemistry, being too long for incorporation in the Proceedings. The report includes results obtained in cooperative work according to various modifications of the provisional methods and a statement of the methods, based on these results, which are recommended for adoption as official at the meeting of 1907.

REPORT ON DISTILLED LIQUORS.

By C. A. Crampton, *Associate Referee.*

Under date of April 14, 1906, the associate referee sent a circular letter to all analysts likely to cooperate in the work. Favorable replies were received from nineteen analysts, two them of arriving too late, and seventeen sets of samples were sent out, accompanied by the following letter of instructions:

May 2, 1906.

Dear Sir: * * * As stated in my circular letter dated April 14, I expect to devote the work this year chiefly to the fusel oil and ethereal salts determinations. The work last year upon the detection of factitious whiskies by methods for artificial coloring was so satisfactory that it does not seem necessary to go over the same ground again.

I will ask you, therefore, to determine the fusel oil in each sample, using both the Roese method and the modified Allen-Marquardt method, adopted provisionally at the last meeting of the association. You will also please use the modified method for esters adopted at the same meeting.

I inclose herewith a copy of Circular No. 26, Bureau of Chemistry, Department of Agriculture, which will give you the newly adopted methods.

Should you have time and material left after making the above determinations, I should be very glad of any further results on the samples, and will leave it to your option to make tests for coloring matter or the routine determinations of alcohol, extract, ash, etc. I would suggest that the determinations of aldehydes and furfural can be made in the distillate which is used for ethereal salts. * * *

Respectfully,

C. A. Crampton,
Associate Referee on Distilled Liquors.

Reports have been received upon twelve sets of samples, and the results are included in the tabulation which follows. As indicated in the circular letter, three samples were sent to each analyst, numbered 1, 2, and 3.

No. 1. Straight Bourbon whisky.

No. 2. Artificial whisky, made by adding coloring matter to alcohol, with an addition of 0.3 per cent by volume of amyl alcohol, or 0.243 per cent by weight.

No. 3. Straight rye whisky.

The following table gives the results obtained by different analysts and the variations and averages. All results are calculated to grams per 100 cc, using 0.810 as the specific gravity of amyl alcohol (fusel oil).

Results of cooperative work on whisky samples.

SAMPLE NO. 1.—BOURBON WHISKY.

Analyst.	Fusel oil.		Esters.	Aldehydes.	Furfural.
	Roese method.	Provisional method.			
G. E. Bolling	0.389	0.170	0.072		
E. M. Chace		.178	.062	0.032	0.001
Edward Gudeman		.226	.083		
Julius Hortvet	.155	.191			
A. Lasché	.243	.167	.069	.005	
L. M. Law	.235	.215	.069		
H. M. Loomis		.309	.070		
O. S. Marckworth		.133	.072	.020	.006
W. B. Pope		.064	.084		
R. E. Stallings	.196	.185	.040	Present.	.001
H. A. Weber	.405				
T. D. Wetterstroem		.132	.079		

SAMPLE NO. 2.—ARTIFICIAL WHISKY CONTAINING 0.243 PER CENT AMYL ALCOHOL BY WEIGHT.

G. E. Bolling	0.389	0.170	0.013		
E. M. Chace		.160	.002	Trace.	None.
Edward Gudeman		.220	.033		
Julius Hortvet	.153	.153			
A. Lasché	.277	.181	.005	0.007	
L. M. Law	.277	.293	.004		
H. M. Loomis			.008		
O. S. Marckworth			.007	.002	None.
W. B. Pope		.138	.014		
R. E. Stallings	.298	.225	.0	None.	0.0
H. A. Weber	.381				
T. D. Wetterstroem		.177	.020		

SAMPLE NO. 3.—RYE WHISKY.

G. E. Bolling	0.462	0.200	0.073		
E. M. Chace		.202	.063	0.033	0.003
Edward Gudeman		.248	.077		
Julius Hortvet	.266	.245			
A. Lasché	.351	.208	.074	.005	
L. M. Law	.214	.259	.079		
H. M. Loomis		.268	.067		
O. S. Marckworth		.179	.085	.018	.013
W. B. Pope		.211	.072		
R. E. Stallings	.260	.255	.044	Present.	.004
H. A. Weber	.389				
T. D. Wetterstroem		.176	.093		

AVERAGES AND VARIATIONS.

Data.	Sample No.	Fusel oil.		Esters.	Aldehydes.	Furfural.
		Roese method.	Provisional method.			
Average	1	0.270	0.179	0.070	0.019	0.003
	2	.296	.191	.010	.002	.000
	3	.324	.223	.073	.019	.007
Highest variation	1	.135	.130	.013	.013	.003
	2	.093	.102	.023	.005	
	3	.138	.045	.012	.014	.006
Lowest variation	1	.115	.047	.030	.014	.002
	2	.143	.053	.010	.002	
	3	.110	.047	.029	.014	.004

COMMENTS BY ANALYSTS.

George E. Bolling: Regarding the Allen-Marquardt method there appears to have been a wholesale loss during some part or parts of the process. Would mercury seals be permissible during oxidation, etc.?

Edward Gudeman: The method for fusel oil was only slightly varied, using 300 cc instead of 100 cc of whisky. Everything else was used in same proportion. The carbon tetrachlorid after washing with the salt solution was made up to 300 cc, and of this 100 cc were used for oxidation and distillation. This was done so as to have identical samples for testing whether the use of tinfoil was necessary and actually took part in the reaction. My results show that the tinfoil does not take part in the reaction and simply acts as protection for the corks.

A. Lasché: Submits a paper giving the results obtained on a number of samples containing known quantities of various fusel-oil constituents by the two methods. This paper is published in full in Lasché's Magazine, September, 1906, page 105.

Following are his conclusions:

The conclusion to be drawn from these investigations, it is apparent, is that the results obtained according to the Allen-Marquardt method do not represent the quantities of higher alcohols or fusel oil contained in distilled liquors, whereas the Roese method results are very reliable and practically correct.

I do not stand alone in my opinion as to the relative merits of these two methods, and see fit to quote here from personal communications received from such distinguished investigators as Prof. Dr. J. Koenig, Münster, Germany, and Prof. Dr. Karl Windisch, Hohenheim, Germany.[a]

I am satisfied that our results are conclusive as to the application of the Allen-Marquardt method for fusel-oil determination in whisky. The Roese method is undoubtedly the most practical and reliable method known to-day and should be retained as the official method for fusel-oil determinations.

L. M. Law: From the results obtained thus far in a study of fusel oil, the provisiona method seems the more promising for obtaining concordant and uniform results. The defect of its giving figures somewhat low can possibly be overcome by finding a factor for the oxidation process which, as is well known, is not a complete one. It is, at any rate, the method for the average analyst with the average laboratory facilities.

H. M. Loomis: The liquors were saponified in all cases by standing cold overnight. Some difficulty was experienced due to foaming in the first distillation, which tannin did not obviate; also found trouble in getting a sharp end point in making the valeric acid solution neutral to methyl orange.

To find whether any loss of valeric acid took place during the eight hours heating in the apparatus used, an experiment was made which showed that no such loss took place during the oxidation process.

O. S. Marckworth: I find the fusel oil method quite tedious, but prefer it to the Roese, providing I can duplicate the results, which I will attempt in the next two weeks. The end point with methyl orange is quite difficult to determine.

R. E. Stallings: The results by the two methods did not agree very closely, as will be seen from the table. It seems that the provisional method (modified Allen-Marquardt) is quite a long and tedious one and there are many chances for error.

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[a] Doctor Koenig says: "Die praktische und auch gleichzeitig zuverlässigste Methode zur Bestimmung von Fuselöl bezw. Amyl-Alkohol in alkoholischen Getränken ist das Verfahren von Roese. Das Verfahren von Allen-Marquardt wird wegen seiner Umständlichkeit kaum mehr gebraucht und *hat auch angeblich manche Mängel.*"

Windisch says: "Ich habe mit dem Verfahren von Roese die besten Ergebnisse bekommen und bin auch Heute noch der Meinung, dass dieses Verfahren besser ist als die übrigen Verfahren, und auch das *Verfahren von Allen-Marquardt.*"

Comments by Associate Referee.

The work was limited this year to a study of the fusel-oil determinations, with the hope of arriving at definite conclusions concerning the reliability of the official methods, but the results are meager and disappointing. Only five of the twelve analysts reporting used both methods.

The figures obtained on the same sample by the different methods vary considerably, but not more so than the results obtained by different analysts with the same method.

Results by the Roese method seem to run high, every analyst except one obtaining results higher than the known quantity in sample No. 2. Results by the Allen-Marquardt method, on the other hand, run low, all the results being below the known quantity in No. 2, except in one case. There seems to be little doubt that the oxidation process in the latter method is not complete. A further study seems to be essential.

The results for esters agree well, except in the artificial whisky, No. 2. From the fact that the process is simply one of distillation and titration in a perfectly clear solution, it would seem that better agreement should have been reached. The method is undoubtedly superior to the previous method, which involved a double titration in a colored solution.

Recommendations.

I have no recommendation to make as to changes in methods. For the ensuing year I would recommend that a further study be made of the determination of fusel oil.

Literature on Fusel Oil.

Results of Fusel Oil Determinations, according to the Allen-Marquardt method as modified by Schidrowitz: Lasché's Magazine for the Practical Distiller, Vol. IV, No. 4, page 105.

The Roese-Herzfeld and Sulphuric Acid Methods for the Determination of the Higher Alcohols—A Criticism: V. H. Veley in Journal of Society of Chemical Industry, Vol. XXV, No. 9, page 398.

No report was received from the referee on vinegar, but the following paper on the subject was presented:

FULLER'S EARTH TEST FOR CARAMEL IN VINEGAR.

By W. L. Dubois.

The fuller's earth test for caramel appears in a number of publications covering methods for food analysis, and has been used quite generally for the detection of added caramel in cider vinegar. In some cases the method has been published with no statement of the precautions necessary in its manipulation, nor the limitations to which it is subject. In order to investigate these points, and if possible prescribe conditions under which it could be applied with certainty, the work described in this article was undertaken.

Fifty samples of pure cider vinegar were obtained from farmers in Pennsylvania through the State Dairy and Food Commission. Of these, eleven were selected, differing as much as possible in physical appearance. Five vinegars made by the author in 1905 were also included in this experiment.

Samples of fuller's earth were procured from several supply houses and from a number of food chemists, the purpose for which the samples were desired being stated. The method was applied as follows:

Fifty cubic centimeters of vinegar and 25 grams of fuller's earth were measured into a 250 cc beaker, stirred thoroughly and allowed to stand one-half hour. The

mixture was then filtered through a dry folded filter, and the color of the filtrate compared with that of the untreated vinegar, filtered in the same way. Color comparisons were made in a Duboscq colorimeter. In the table below the results are expressed as per cent of the total color removed by fuller's earth. The last five vinegars in the table were made by the writer.

Amount of color removed by 9 samples of fuller's earth from vinegars.

Vinegar, Nos.	Fuller's earth numbers.								
	15663.	15664.	17038.	17039.	17040.	17042.	17043.	17045.	17080.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
17046	29.6	38.0	24.0	44.8	28.0	31.2	18.4	50.0	.....
17047	41.9	46.8	48.0	60.0	42.0	42.0	43.2	50.0	.....
17048	34.0	20.0	30.0	44.0	22.2	25.0	25.0	4.2	.....
17049	.....	31.6	0.0	20.0	0.0	20.0	0.0	0.0	0.0
17050	20.0	36.7	0.0	4.0	0.0	23.3	0.0	.....	48.3
17055	0.0	0.0	7.7	52.0	20.0	36.8	33.3	40.5	.....
17056	70.8	68.0	67.9	70.0	66.0	60.7	66.6	66.6	71.4
17057	.....	28.0	27.2	32.0	12.0	20.0	0.0	30.0	45.5
17058	.....	40.0	25.0	25.0	24.0	36.0	4.0	20.0	71.9
17059	.....	44.0	20.0	30.0	4.0	10.0	25.0	23.1	.....
17060	56.2	63.1	65.0	66.6	63.1	53.3	63.1	67.6	.....
17512	.....	.....	.....	57.9	42.9	0.0	35.9	63.4	.....
17513	.....	.....	.....	43.4	24.7	16.7	21.8	66.6	.....
17514	.....	.....	.....	41.2	13.0	0.0	0.0	50.0	.....
17515	.....	.....	.....	37.5	0.0	.....	11.0	.....	.....
17516	.....	.....	.....	41.2	37.5	38.9	32.5	57.6	.....

Discussion of Results.

The color removed from pure cider vinegar by fuller's earth varies, according to the figures in the table, from none to 72 per cent. No one sample of fuller's earth can be selected from the above as giving uniform results. For instance, Nos. 15663 and 15664 remove no color from vinegar No. 17055, thereby indicating that it is pure, while from vinegar No. 17056, which is just as pure as No. 17055, 71 per cent and 68 per cent, respectively, of the color are removed.

Vinegar No. 17050 would be indicated as pure by treatment with earths Nos. 17038, 17040, and 17043, while its quality would be doubtful according to earth No. 15663 and condemned by No. 15664. Again, earths Nos. 17038, 17040, 17043, which give uniform results on vinegar No. 17050 and comparable results on several others, are at wide variance on vinegar 17057. Earth No. 17080 is one received from a chemist who uses this test and declares it reliable if 25 to 30 per cent be allowed for the color which fuller's earth will remove from pure vinegar. As shown in the table, it removes from one sample of pure cider vinegar no color at all, while taking out as much as 72 per cent of color from another sample. There seems to be no uniformity in the data, and it is impossible to select any one of the fuller's earths tried which could be relied upon to give truthful results. In the writer's estimation the method is unreliable, and should only be used as a preliminary test. If no color, or only a small percentage of color, be removed, the analyst is reasonably safe in pronouncing the sample pure. On the other hand, if all the color disappears he is equally secure in declaring caramel present. But for the large number of vinegars which lose from 25 to 75 per cent of their color when treated with fuller's earth the data obtained by this test are not final, and it is necessary to subject the vinegar to further treatment before a conclusion regarding the presence of caramel can be reached.

Mr. Crampton. The fuller's earth test for caramel in vinegar, as published by Mr. Simons and myself some time ago, was put forth only in a tentative way, as it had been used mainly upon distilled spirits and not applied to many samples of vinegar. This paper is the first report I have heard of any extensive work being done with

the method as applied to vinegars, and I think undoubtedly the test should be considered only as corroborative and be accompanied by other tests.

REPORT ON FLAVORING EXTRACTS.

By E. M. Chace, *Associate Referee.*

The work for the past year has been confined to testing the proposed methods on the determination of the aldehydes (citral) in lemon oils and extracts. The following methods were given a preliminary trial by the referee: Sadtler's,[a] Romeo's [b] modification of Sadtler's, and Berte's.[c] Of these, Sadtler's gave promise of being the best. The method, in brief, is as follows:

Five to 10 grams of the oil are weighed into an Erlenmeyer flask and, after neutralizing, 25 or 50 cc of a 20 per cent solution of neutral sodium sulphite are added. Rosolic acid or phenolphthalein may be used as indicator. On mixing the oil and sulphite solution a red color immediately forms, owing to the alkali set free by the reaction. This is neutralized with half-normal hydrochloric acid from time to time, the flask containing the mixture being surrounded by boiling water. The reaction is complete in about half an hour. The citral is found from the amount of acid used to neutralize the alkali set free according to the following reaction:

$$C_9H_{15}CHO+2H_2O+2Na_2SO_3=C_9H_{15}CHO(NaHSO_3)_2+2NaOH.$$

The method has two serious defects: (1) The alkali formed must be neutralized immediately, or at the temperature of boiling water it attacks the aldehyde sulphite compound regenerating citral; and (2) the end point is obscure on account of dissociation of the sulphite in solution. On this account the final neutralizing must be done in the cold. With the unmodified method it was impossible to obtain concordant results.

It was found that the delicacy of the end point could be considerably increased by the addition of salt to the solution, but even then the results seemed uniformly low, although the greatest care was used in neutralizing the alkali as soon as formed.

The following results were obtained on solutions of citral in alcohol:

Determinations of citral in alcohol solutions (Sadtler's method).

Amount added.	Amount recovered.	Percentage recovered.
Grams.	*Grams.*	*Per cent.*
0.500	0.366	73.2
.215	.206	96.0
.510	.479	92.0
.510	.444	87.0
.510	.401	80.0

Samples made up in limonene, upon which the citral had been previously determined by the same method, gave correspondingly low results.

The modification of this method by Romeo consists in using a solution of potassium acid sulphite (the acidity of which equals the alkalinity of half-normal alkali) to neutralize the alkali formed. After neutralizing the sodium sulphite, a definite volume—about 20 cc—of the potassium acid sulphite is first added and then the neutralized lemon oil. This mixture is heated on the water bath under a reflux cooler, with frequent shaking for three hours, is then removed, cooled, and the excess of acidity due to the unneutralized potassium acid sulphite titrated with half-normal sodium

[a] J. Franklin Institute, December, 1903; February, 1904.
[b] Chem. and Drug., 1905, 408.
[c] Chem. Ztg. *29*, 805, Abs. in Analyst, October, 1905.

hydroxid. In this way the method overcomes the error due to the presence of free alkali, but it still retains the difficulty of an obscure end point.

Fair results were obtained when solutions of pure citral were used and sodium chlorid added before titrating.

Results using chemically pure citral and adding sodium chlorid.

Amount added.	Amount found.	Percentage found.
Grams.	*Grams.*	*Per cent.*
0.540	0.531	98
.525	.549	105
.510	.534	105
.525	.554	.....
.538	.527	.....
.486	.496	.....

The method failed completely, however, when the citral was added to limonene solutions. Thus a mixture of limonene and citral, theoretically containing 6.62 per cent of citral, gave 5.72 per cent, 7.02 per cent, 5.23 per cent, and 5.86 per cent.

Berte's method depends upon the polarization of the oil before and after the removal of the citral by potassium acid sulphite. Ten cc of the oil are emulsified with 50 cc of potassium acid sulphite and heated for ten minutes on the water bath, cooled, re-emulsified, heated for five minutes, cooled, and the oil separated by means of a separatory funnel. It is then thoroughly washed and dried by shaking with anhydrous sodium sulphate. The original oil and this citral-free oil are now polarized at the same temperature and the citral calculated by the following formula:

$$C = \frac{100\,(B-A)}{B}$$

in which A is polarization of the original oil, B the polarization of the citral-free oil, and C the per cent of citral. Only negative results were obtained by this method; the citral apparently is not removed by the treatment.

No methods depending upon the use of the cassia flasks were tried, as the consensus of opinion seems to be that those methods do not give accurate results on lemon oil, owing either to the resins present or to the fact that the citronella aldehyde present forms a sulphite compound which is insoluble in water.

A method depending upon the reduction of ammoniacal silver nitrate was also tried, the results being uniform where citral alone was used, but very irregular on mixtures of limonene and citral.

The method finally adopted for collaborative work was a modification of that of Medicus,[a] and the following instructions[b] and samples were sent to the eight chemists who had expressed a desire to collaborate.

A was a commercial lemon oil.

B was a solution of c. p. citral in unpurified alcohol containing 0.25 per cent by weight.

C was a solution of limonene containing 0.12 per cent of citral.

D was an extract made by adding 5 grams of A to 100 grams of alcohol.

The instructions sent with the samples were as follows:

[a] Forschungs-Berichte über Lebensmittel. 1895, *2*: 299.

[b] See also J. Amer. Chem. Soc., 1906, *28*: 1472.

COLORIMETRIC METHOD FOR THE DETERMINATION OF CITRAL IN LEMON EXTRACTS.

Reagents.

Standard citral solution.—Made by dissolving 1 gram of c. p. citral in 1 liter of 50 per cent alcohol.

Fuchsin solution.—Dissolve one-half gram of fuchsin in 100 cc of water and add a sulphurous acid solution containing 16 grams of SO_2. Allow to stand until the color disappears and make up to 1 liter. This solution deteriorates on long standing.

Aldehyde-free, 95 per cent alcohol.—Various methods may be used for purifying the alcohol. The following method gave the best results in this laboratory:

The alcohol is allowed to stand over caustic alkali for a day or two and is then distilled. This distillate is boiled for three hours under a reflux cooler with 25 grams per liter of meta-phenyl-diamine-hydrochlorate and finally distilled. The purified alcohol gives only a trace of color when treated with the fuchsin solution at 15° C.

Note.—All reagents must be cooled to about 15° C., and used at that temperature. While it is not necessary that they be kept at exactly 15°, they must all be kept at the same temperature. A cooling bath such as is described by Given[a] is used in this laboratory. This bath gives abundant room for all reagents and comparison tubes.

Manipulation.

Approximately 2 grams of lemon oil are weighed in a small flask, transferred with alcohol to a 100 cc flask, and made up to the mark with alcohol at the temperature of the cooling bath. (For lemon extracts, weigh 20 grams and make up to 50 cc.)

It is well to make up a second solution after calculating the first, so that this solution shall have the same strength as the standard, i. e., 1 mg per cubic centimeter, and to do the final work on this.

In making up the standards and samples for comparison, add first the lemon product or citral, next 20 cc of aldehyde-free alcohol, then 20 cc of fuchsin solution, and finally make up to the 50 cc mark with alcohol. Allow to stand in the cooling bath for ten minutes, and read.

Four milligrams are preferred as a standard to use with colorimeters, and 2 mg where comparisons are made in Nessler tubes. Final comparisons should be made on solutions of approximately the same depth of color, as the increase in color is not exactly proportional to the amount of citral present. Calculate the results as per cent by weight.

The samples sent are as follows: A, lemon oil; B, citral solution; C and D, lemon extracts. The method has given very satisfactory results on lemon extracts; on lemon oils it is but fair, owing to the great multiplication of the error. Working with alcohol of such high percentage it is very evident that temperature is a factor which must be closely watched. In this laboratory we cool even the pipettes before using them. The time given for developing the color (ten minutes) is optional; fifteen minutes may be used. The essential requirement is that the standards and samples should stand the same length of time at the same temperature.

But four reports were received, one of the collaborators having worked under conditions so widely different from those prescribed by the method that his results have not been tabulated.

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[a] J. Amer. Chem. Soc., 1905, *27* (12): 1519.

Cooperative work on the determination of citral in lemon extracts (colorimetric method).

Analyst.	Samples.			
	A.	B.	C.	D.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Geo. E. Bolling, sewer, health, and water department, Brockton, Mass	6.40	0.80	0.18	0.28
A. F. Seeker, food inspection laboratory, port of New York	4.53 5.00	.275	.115	.23
H. J. Holland, food inspection laboratory, San Francisco, Cal.	(a)	.312	.147	.217 .258
E. M. Chace, associate referee, Bureau of Chemistry, Washington, D. C.	5.29 5.02 5.16	.282 .284 .279 .282	.134 .134 .121	.262 .267 .280 .264 .277

[a] Not reported.

It is recommended that the collaborative work on the method be continued for another year.

REPORT ON BAKING POWDERS.

By W. M. Allen, *Associate Referee.*

As no recommendations regarding the work on baking powders and baking chemicals for this year were made in 1905, it was the intention of the associate referee to take up the recommendations made in 1904, but owing to other duties this work was reached too late for cooperative investigation. The referee had a large number of baking powders on which the available carbon dioxid was to be determined, the total and residual not being required except to give the available by difference, and as these determinations were to be made in duplicate it was deemed advisable to devise some method for determining the available carbon dioxid directly, without making the total and residual determinations. For this purpose the following method, based on the method of McGill and Catlin for the determination of the residual carbon dioxid as described by Winton in the Provisional Methods for the Analysis of Foods,[a] was tried:

DETERMINATION OF AVAILABLE CARBON DIOXID WHEN THE TOTAL AND RESIDUAL AMOUNTS ARE NOT REQUIRED.

Weigh 2 grams of the baking powder into a dry flask of about 150 cc capacity, and attach the flask to a Heidenhain's apparatus for the determination of carbon dioxid. Through the funnel tube, which must have a stop cock, run into the flask containing the sample about 30 to 40 cc of cold water. The condenser of the apparatus, to which the flask is attached, should have some little play so that the flask may be shaken with a slight rotary motion until the sample is thoroughly mixed with the water. Place the flask in a small water bath, filled with cold water, by raising the bath up under the flask until the latter is about half submerged. The water bath should be just large enough to conveniently accommodate the flask. Heat the bath to boiling, taking about eight to ten minutes to reach that temperature, so that the heat in the flask will be gradual. Continue the boiling until the sulphuric acid in the indicator of the apparatus begins to recede, showing that the operation is complete. Then attach and start the aspirator and open the funnel tube, which should be guarded by a soda-lime absorption tube.

Complete the determination as directed under total carbon dioxid, Provisional Methods, Bulletin No. 65, above mentioned, page 98, using the precautions there noted.

By this method results agreeing closely with those given by the provisional methods are obtained. If the amounts of residual and total carbon dioxid are required, the determinations are completed as follows:

[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, p. 104.

RESIDUAL CARBON DIOXID.

After the available is determined and the soda-lime absorption tubes are replaced in the apparatus, run into the flask containing the sample about 40 cc of hydrochloric acid (sp. gr. 1.15) to set free the residual carbon dioxid. Boil the acid very gently for a few minutes, and complete the determination as above directed under available carbon dioxid.

TOTAL CARBON DIOXID.

To obtain the amount of total carbon dioxid, add the residual to the available.

The analytical results obtained in the trial of this method are given in the following table:

Comparison of the determination of available carbon dioxid in baking powders by the direct and the provisional methods.

Sample.	Available carbon dioxid.		Sample.	Available carbon dioxid.	
	Provisional method, by difference.	Direct method.		Provisional method, by difference.	Direct method.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
Cream of tartar baking powder, starch filler	12.29	12.20	Alum baking powder, starch filler	15.90	15.78
	11.37	11.40		10.99	10.92
	11.40	11.36		8.01	8.07
	12.21	12.18		10.99	10.92
Phosphate baking powder, starch filler	9.54	9.60	Alum-phosphate baking powder, starch filler	11.22	11.24
	13.54	13.58		10.55	10.54
	9.74	9.70		8.01	8.03
	10.26	10.18			

REPORT ON FATS AND OILS.

(Cooperative work on the cloud and the cold tests for 1905 to 1906.)

By L. M. Tolman, *Associate Referee.*

This work was begun two years ago by sending out a preliminary circular giving the various methods used in different laboratories, asking for suggestions. It was found that three general types of methods were in use for making the so-called cold test:

(1) The cold test as practiced for cotton-seed oil used for salad purposes, in which the oil is placed in a bottle and allowed to stand at a definite temperature for a definite time, when there must be no formation of crystal and the oil must be perfectly clear.

(2) The cloud test as practiced in the Armour laboratories, in which the temperature at which the first cloud is formed in the oil as it is cooled is determined.

(3) The flowing test, in which the temperature at which an oil which has been frozen will flow under definite conditions is determined.

These tests are evidently quite different, they have different objects in view, and should have different names, and it has been suggested that the following nomenclature be used: The first test to be called the cold test; the second, the cloud test; and the third the flowing test. These names are suggestive, and will be adopted in the future in this work unless some reason is suggested for a change.

In a second circular sent out this year a summary of the suggestions that had been made was given, and the following methods were offered for trial, four samples of oil being sent to each of the collaborators:

CLOUD TEST.

The cloud test is given by Mr. Manns as follows:

(1) The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding point is reached.

(2) The oil must be heated to 150° C. over a free flame, immediately before making the test.

(3) There must not be too much discrepancy between the temperature of the bath and the clouding point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in a bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice, and water.

The test is conducted as follows: The oil is heated in a porcelain casserole over a free flame to 150° C., stirring with the thermometer. As soon as it can be done with safety, the oil is transferred to a 4-ounce oil bottle, which must be perfectly dry. One and one-half ounces of the oil are sufficient for the test. A dry Fahrenheit thermometer is placed in the oil, and the bottle is then cooled by immersion in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The bottle is frequently removed from the bath for a few moments. The oil must not be allowed to chill on the sides and bottom of the bottle. This is effected by constant and vigorous stirring with the thermometer. As soon as the first permanent cloud shows in the body of the oil, the temperature at which this cloud occurs is noted.

With care, results concordant to within 1° F. can be obtained by this method. The Fahrenheit thermometer is used merely because it has become customary to report results in degrees Fahrenheit.

The oil must be tested within a short time after heating to 150° C., and a re-test must always be preceded by reheating to that temperature. The cloud point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

COLD TEST (MILLWOOD).

Warm the oil until all the stearin is dissolved and filter, through several thicknesses of filter paper, into a *dry* 4-ounce wide-mouth bottle, 1½ ounces of the oil to be tested; place in a freezing mixture and stir until the oil becomes solid, then cork and leave for one hour in the freezing mixture. Take the bottle from the freezing mixture, wipe it dry, and place in a holder of ordinary magnesia, asbestos pipe covering, or any suitable holder which will insulate the sides of the bottle. The frozen oil is broken up and well stirred with the special cold-test thermometer previously described, and at every degree rise in the temperature the bottle is inverted; continue till the oil will run to the other end of the bottle. The temperature registered at this stage is to be considered the cold test.

The following list of questions was submitted:

For lubricating oils:

(1) Method to be used:
  (*a*) A flowing test?
  (*b*) A clouding test?
(2) Preparation of oil for analysis:
  (*a*) Shall it be dried, and how?
  (*b*) Shall it be filtered?
(3) Method of cooling:
  (*a*) Shall it be stirred until solid?
  (*b*) Shall it stand a definite time; and if so, how long?
(4) Method of melting:
  (*a*) Shall it be allowed to warm at room temperature?
  (*b*) Shall it be warmed in a bath?

As regards salad oils:

Can the cloud test be used for the testing of salad oils, such as winter cotton-seed oil?

The samples submitted for the work were prime lard oil, neatsfoot oil, grease oil, and tallow oil. The collaborators were requested to test them as follows:

(1) By the method in use in the respective laboratories.
(2) By the cloud test as given by Mr. Manns.
(3) By the cold test of the Pennsylvania Railroad, as modified by Millwood.
(4) In regard to the other points at issue as far as is practicable.

The need of a special thermometer which can be read without removing from the bottle was noted by Robert Job, of the Philadelphia and Reading Railroad, and by J. P. Millwood, of the Brooklyn Navy-Yard. The latter thus describes the thermometer used by him: "The special thermometers used are graduated in degrees from 0° to 100° F. and are 18 inches long, with the zero point about 7 inches above the bulb, which brings it outside the bottle."

The following table gives the results reported by the twelve men who sent in their results:

Results on cloud and cold tests, 1905–6.

Analyst.	Cloud test.				Flowing test (Millwood).			
	1. Prime lard oil.	2. Neat's-foot oil.	3. Grease oil.	4. Tallow oil.	1. Prime lard oil.	2. Neat's-foot oil.	3. Grease oil.	4. Tallow oil.
	°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.
A. V. H. Mory	24 –26	13 –15	51 –53	72–74	46	30	45	75
Robert Job	30	.....	.....	.....	28	5	46	56
Max H. Wickhorst	.....	.....	.....	.....	45	8	40	83
W. E. Tinney	25 –27	15 –17	50 –52	73 –75	45. 5	33. 5	48	78
A. G. Manns	25 –27	15 –17	49 –51	72 –74	44 –46	30 –32	52 –54	70 –72
R. D. Oilar	29. 5–33. 5	17. 6–18	61. 8–63. 5	76 –78	43. 5–45	28. 4–32	40 –42	82. 4–83. 4
W. D. Richardson	27 –28	15. 5	51	74	46. 5	31	43	84
Wilson Low	30	18	.....	.....	46	33	.....	.....
C. F. Hagedorn	24 –26	14 –16	51 –53	73–75	44	31	45	75
J. E. Weber	26. 6–28. 4	15. 8	58 –59	76	46. 4	.....	57. 2	80. 6
J. P. Millwood	29	23	48	76	44	36	41	75
A. H. Schmidt	30. 2	23	60	76	42	30. 2	44. 6	82. 4
A. Lowenstein (1)	29 –29. 5	18	57. 5–58. 5	77	45 –46	30. 5–31. 5	48. 5–49. 5	79 –80
A. Lowenstein (2)	29 –30	15 –16	55 –56	75–76	46 –47	29 –30	45 –46	83 –84
Maximum	33. 5	23	63. 8	78. 0	46. 5	36. 0	57. 2	83. 4
Minimum	24. 0	13	49. 0	72. 0	28. 0	5. 0	40. 0	56. 0
Difference	11. 5	10	14. 8	6. 0	18. 5	31. 0	17	27. 4

FLOWING TEST.

A. H. Schmidt [a]	.....	.....	.....	.....	19. 4	9. 2	37. 4	48. 2
A. Lowenstein [b]	.....	.....	.....	.....	45 –46	32 –33	53 –54	69 –70
					45 –46	32. 5–33. 5	53 –54	69 –70

[a] Congeals sample in a test tube. [b] Sample frozen over night.

The following are the comments and answers given by the various analysts:

Comments of Analysts.

A. G. MANNS.

Cold test.—In the case of prime lard oil, no difficulty is encountered in obtaining concordant results on the cold test. Different portions of the same oil were tested under different conditions and the results agreed to within one degree. One portion was frozen hard and the flowing point taken; another portion was kept in a cooler having a temperature of —100° F. for three days, and no difference in the cold test was noted.

Yellow grease oil gives a wide variation of results under different conditions of testing. One portion of a sample tested in the ordinary way gave a cold test of 39°–41° F. at a room temperature of 78° F. Another portion frozen under the same conditions along with the first sample gave a test of 46°–48° F. at a room temperature of 56°. Still another portion of the same sample, after having remained for two days in a freezer at a temperature of —10° F. gave a cold test of 49°–51° F. Thus a variation of 10° F. was obtained on the same sample. The result is greatly influenced by the length of time and temperature of freezing, and the temperature of the room in which the test is made.

Tallow oil shows the same variation under different conditions, and in the case of this oil a room having a very high temperature must be used in order to obtain the flowing point, or artificial heat of some kind must be employed.

Concordant results were obtained in testing extra No. 1 lard oil, when precautions were taken to use the same room temperature and the same conditions of freezing.

These results show that a different set of specifications must be used for each variety of oil to be tested, and these specifications must be made very rigid.

Cloud test.—The cloud test gives perfect satisfaction in the testing of all oils met with in the everyday practice of the packing-house and refinery business.

In this method a perfectly defined starting point is specified, a perfectly defined cooling medium is given, and a definite end point is given. No difficulty is encountered by different observers in obtaining a close agreement on the cloud point, and the method has the advantage of speed and convenience, so necessary where a large number of determinations must be made daily.

There seems to be no direct relationship between the cloud test and the cold test. The cloud test is based on the solubility of the stearic constituents in the accompanying palmitic and oleic constituents. The cold test is founded on the viscosity of the combined constituents. The relationship between these two properties expressed in degrees of temperature is not constant, because of the varying proportion of the three constituents in different grades of oil.

The Millwood test, while it gives exact conditions for freezing the oil, makes no provision for the temperature of the room in which the test is carried out.

As our experiments show, this factor enters largely into the result, and while it does not affect the test in the case of prime lard oil it varies the results greatly in the case of several other oils.

We would answer the questions on page 30 in the following manner:

(1) The cold test would be the more desirable if rigid specifications could be drawn up to cover the questions of length of time and temperature of freezing and of the room temperature. We believe the test to be impracticable, however, because the specifications would have to take into account oils flowing at such a low temperature that it would require a very expensive and unusual equipment to have rooms in which the test could be carried on. There might be two specifications: one for oils flowing at a high temperature, and one for oils flowing at a low temperature. That would make the former a practicable test. The method, too, must always be a lengthy and inconvenient one, especially as a factory method.

(2) (*a*) It should be heated rapidly over a free flame to 150° C. (*b*) It should be filtered if not clear when hot.

(3) (*a*) It should be frozen rapidly without stirring, and then be allowed to stand in the freezing bath for the requisite length of time. (*b*) The oil must be frozen very hard throughout; after it is once in this condition, which will require several hours at least, it makes no difference in the result how much longer it is frozen. The length of time of cooling would vary greatly with the grade of oil used.

(4) (*a*) It should be allowed to warm up gradually at a specified room temperature. (*b*) A warming bath would heat the frozen oil superficially through the sides of the

bottle, and allow the whole mass to flow to the other end of the bottle at a temperature much below the flowing point of the whole mass.

In answer to your question about the test for salad oils, we think the cloud test should be used.

A. V. H. MORY.

Mr. Mory also notes that the flowing test gives very different results when the conditions of analysis are varied; and that the oil should be dried and filtered. He objects to the stirring of the oil in the flowing test while the oil is being cooled, as air bubbles are introduced, which affect the results. He thinks that it would be very difficult to so regulate the conditions of the flowing test that it would be satisfactory, and says regarding the use of the cloud test for salad oil: "I think the cloud test is the proper one to be used. It should be remembered, however, that the test gives only a relative idea of the temperature at which an oil will cloud on long exposure."

Mr. Mory considers the cloud test the most satisfactory for all purposes, being less subject to conditions.

MAX H. WICKHORST.

(1) For railroad purposes, the clouding test is probably of little service, and probably what is needed is the flowing test.

(2) I should be in favor of making the cold test on oil as received, without drying or filtering, as the oil is used in the condition in which it is received.

(3) I do not feel that I can express an opinion with much positiveness, but it would seem desirable to stir the oil until solid, so as to avoid any serious segregation.

(4) It would be most convenient to warm up simply by exposing the bottle wrapped with asbestos or other material to ordinary room temperature; in case of such oils as tallow, a higher temperature must be used. Whether exposure to room temperature gives the best or most accurate results, I am not prepared to say.

W. D. RICHARDSON.

(1) (*a*, *b*) Both tests are of value depending on the use of the oil.

(2) Dry but not filter sample for cloud test. Dry over flame to 110° C. till free from moisture.

(3) (*a*) Yes. (*b*) Must stand from one-half hour to one hour in freezing mixture to be thoroughly chilled.

4. (*a*) Yes. Oils flowing below room temperature. (*b*) Oils flowing above room temperature must be warmed up slowly in an air bath with continuous stirring.

J. P. MILLWOOD.

(1) A flowing test only is necessary, as a clouding test will reveal nothing in regard to its value as a lubricant.

(2) The oil should be examined undried and filtered, as this is the condition in which it will be used.

(3) It should be left at rest until solid, as the frequency and rapidity of stirring is liable to introduce a personal equation, and, furthermore, in actual use it is at rest in an oil cup or oiling can. In order to get concordant results, standing a definite time is necessary. We find one hour sufficient.

(4) For oils normally liquid, room temperature is sufficient. A bath of warm water is necessary for fats and greases.

J. E. WEBER.

(1) Method: Use "flowing test."

(2) Preparation of oil for analysis: Heat the oil to 150° C., but filter only when the oil is not clear.

(3) Method of cooling: Stir the oil until almost solid, then start the test right away.

(4) Method of melting: Let the oil warm up by placing the bottle in a holder of magnesia asbestos pipe covering. It is very convenient.

ROBERT JOB.

(1) With the ordinary lubricating oil we have never found necessity for the clouding test, since the result of the cold test gives the desired information as to properties in service.

(2) If oil contains moisture or dirt it is desirable to filter.

(3) As stated above, we find that it is unnecessary to stir until solid; also that the time of standing after once becoming solid is immaterial.

(4) As to melting, we think it preferable to warm up at room temperature.

R. D. OILAR.

It is apparent that drying a sample before testing does affect the results. The drier the sample the lower the "cloud test," and the writer disagrees with Mr. Manns on this point. The sample should be heated for a few minutes, to a point where it is known that all crystallized glycerids of the fat, visible or invisible, are melted, somewhat as is required by the New York Produce Exchange method on winter cottonseed oils, but not to 150° C.

The drying of the sample would create false conditions—that is, if a commercial sample is tested and clouds at a higher temperature than the guaranty, it matters not to the consumer whether the *sample* is wet or dry; the clouding at the undue temperature remains the same, whereas if the sample were dried, its cloud test might be strictly up to grade; however, the consumer is obliged to use the oil which *does actually cloud* at this temperature for which the chemist's report would be "O. K." if tested on the dried sample.

The writer would recommend a flowing or "cold test" for lubricating oils and a "cloud test" for edible oils.

Samples should be neither dried nor filtered before testing, for reasons given above.

The writer has not experimented on the time that the sample should remain in the freezing mixture, but it seems that an hour would be sufficient, especially if a uniform test is to be adopted.

The melting should be effected in an insulated receiver, such as is described above for melting at low temperature, or heated in a water bath for higher tests.

It seems probable that a concise "cloud test" may be devised for winter cottonseed oil, whereby a given bulk of oil at a given temperature will be placed in an air bath of given dimensions and of a given temperature, which would be equivalent to the five-hour test now required by the New York Produce Exchange, and if specifications were adhered to very closely the time would not enter into the problem.

It is quite apparent that conditions control the results on any of the above tests, and specifications are necessary as to temperature of cooling baths, volumes, etc.

[R. D. OILAR made a more complete study of the question, and the following table gives the results of his work with the cloud test]:

Special study of the cloud test (Oilar).

Sample.	Stirring as the oil is cooled.			Not stirring as the oil is cooled.	
	Temperature of clouding.	Temperature of bath.	Remarks.	Temperature of clouding.	Temperature of bath.
	° C.	° C.		° C.	° C.
1	33.4	.....	Reheated to 150° C.	36–37.5	32
	30.6	17.6		33–34	21–23
	29.5	17.6			
	29.8–30.2	14–17.6			
3	63.5	57–59	Lower reading due to colder bath.	64–66.2	59–64
	60.4	51–55			
4	78	75.2		82–84	77–78.8
	76.5	64—68			

[The figures show that a higher cloud test is obtained by allowing oil to remain quiet during the test. The following table gives his results on the flowing test]:

Special study of the flowing test (Oilar).

Sample.	Stirring as the oil warmed. (Millwood.)			Not stirring as the oil warmed.	
	Flowing test.	Temperature of bath.	Remarks.	Flowing test.	Temperature of bath.
	° C.	° C.		° C.	° C.
1	43.5–45	Room temperature.	Cooled until very hard.	48.2	50
3	40–42	.....do.....	.....do.....	61.5	62.6
4	82.5–83.5	.....do.....	Warmed in hand.	85.2	100.4

[This study shows that results are much higher when the oil is not stirred as it melts, and all the data indicate that the methods used must be followed very closely as to details in order to obtain any satisfactory results.]

A. H. SCHMIDT.

In the Millwood test I found the lard oil to flow at +5.5° C., whereas when placed in a test tube, immersed in a freezing mixture, and constantly stirred with the thermometer, it still flowed at −3.0° C. The same general results were obtained with the other oils.

I also believe that the Millwood test is not the correct way of testing a lubricating oil, as that is really the point at which a frozen or rather solidified oil becomes semifluid, whereas the cold test for a lubricating oil should be to determine at what temperature the oil ceases to fulfil its function as a lubricator by congealing, and I found that to be much lower in most cases than is indicated by the Millwood test.

A. LOWENSTEIN.

(1) It is our opinion that a flowing test should be used for lubricating purposes, and a cloud test for edible oils.

(2) If the oil when melted is perfectly clear, I do not think that it needs to be further dried. If when melted it is turbid or contains suspended matter, it should be filtered through several thicknesses of filter paper, and if still turbid should be dried by heating to 105° C. until all moisture is removed.

(3) (*a*) If stirred at all, it should be stirred until it is solid, and the temperature of the bath should be so low and (*b*) it should be left in the bath so long that there will be absolutely no question that the oil is solid. I think that the temperature of the

bath is here the most important consideration, and upon it the length of time which the oil remains in it depends. With the bath at 15° F. below zero one hour will suffice, but for higher temperature a longer time is required, especially for oils of such low cold test as winter-pressed neat's-foot oil.

In our regular method we do not stir the oil at all, but place it direct in a "freezer" at a temperature of —5° F. and allow it to remain overnight. If you will examine the results on tallow oil obtained by Millwood's method and the one employed in this laboratory, you will note a difference of 10°, and the way we account for this is that in stirring or agitating while chilling, a large amount of air is worked into the oil, and you get very much the same effect as in the agitation of soap or lard or cream. In the case of lard, for example, one which has a titer of 37.5° C., and which has been agitated thoroughly will hold up in a warm room better than a lard having a titer of 38.5° which has been chilled without agitation. In oils containing a smaller percentage of stearin this difference is not so noticeable, and in the case of neat's-foot oil and lard oil the results obtained by the two methods check quite well. I do not think that oils of cold tests over 40° F. need to be stirred while chilling, as there is ample time to render the mixture homogeneous by stirring when making the flowing test.

(4) (*a*) I do not think the oil should be allowed to warm up at room temperature.

(*b*) A bath would be satisfactory, but would have to be different for each kind of oil. A bath a few degrees lower than the cold test of the oil would, I think, be satisfactory. In the case of oils of very low cold test, these should be run very quickly after removing from the freezing mixture, otherwise the oil will melt next to the walls of the bottle and make it difficult to get the proper flowing test.

If the cloud test is used, the bottle should have an air jacket and not be placed directly in the bath. It is quite difficult in some cases to prevent the oil from freezing to the sides and bottom of the vessel.

Comments of the Referee.

The results obtained as shown in the table are certainly very divergent, considering the details given in the instructions, and show that, as the methods have been described, some essential directions are lacking or the personal equation is too large to make them of any value, when two men, following exactly the same method, can differ 31° F. in determining the point at which an oil flows from one end of a bottle to the other. That the personal equation does enter largely is shown by one analyst obtaining the lowest results in three out of the four samples. The same tendency may be noted in the highest results.

The following curious point is also brought out: The temperature at which the cloud forms in cooling an oil down in most of the oils is several degrees below that at which the oil flows when being melted after cooling. That is, under the methods employed the oil is liquid and clear below the temperature at which it flows on being melted. For example, lard oil clouds at 30.2° F., congeals at 19.4° F., and on remelting flows at 42° F.

It is, however, true with nearly all substances that the crystallizing point is below the melting point, but with the grease oil this is not the case, the crystallizing point being above the flowing point.

Time is perhaps the most important factor. As has been shown in the determination of melting points of fats, it is necessary to allow them to stand a number of hours after they have been melted and recooled before the correct melting point is obtained, and the same fact is doubtless true in this determination, and also in the melting point it is necessary to allow the temperature to rise very slowly in order to obtain anything like the true melting point, and if this is true in melting points of pure compounds it certainly must be true in such a determination as this.

It seems to the referee that before the flowing test can be of any value some method of warming up the frozen fat must be employed, such as suggested by Lowenstein.

who takes the sample from the freezer and places it in a bath at about 40° for fifteen minutes, so as to allow it to soften, then stirs until it flows. This procedure, of course, could not be employed with oils with a flowing test below 40° F. Some arrangement of this kind, varied in temperature somewhat for the different oils, seems necessary from the results obtained this year. This might be accomplished as follows:

After the oil has been frozen (and the temperature of the freezing bath should be well below that of the melting point of the oil so that it is frozen hard) the sample is placed in a water bath 5° to 10° below the flowing test and allowed to warm up to that temperature. Then finish its determination as now directed.

As to the clouding test, it seems to be shown that there is no relation between the flowing point of an oil and the temperature at which an oil clouds, and as the former is the question in lubricating oils, it would seem that the cloud test is hardly applicable.

The consensus of opinion of the collaborators seems to be that this test is of value only on salad oils. The results obtained with the cloud test on the various oils were more uniform, as given in the table, showing that the method used gives comparable results, although the maximum and minimum show a wide variation, due to the freezing of the oil on the sides of the bottle. This might be obviated, as suggested by Mr. Lowenstein, by surrounding the bottle with an air jacket, so that the walls of the bottle do not come in direct contact with the cold bath.

Summary.

The work on fats and oils this year is a continuation of that begun last year on the cold test and is of a preliminary nature. Considerable cooperative work has been done, fourteen men sending in reports on the samples. The results, while not agreeing in a satisfactory way, have brought out a number of important points, and will enable the referee to continue the work with a clearer idea of what is necessary. The results showed that there were two entirely different tests known as the "cold test," and names have been given to these which will in the future distinguish them from each other.

It was clearly shown that the cloud test and the flowing test are dependent on different factors and can not be used for the same purpose, and that the flowing test is the one which is of value in lubricating oils, while the cloud test is more applicable to salad oils.

The results also showed the need of more definite, detailed directions for the flowing test, indicating that it will be necessary to warm up the fats in a bath in which the temperature can be controlled. It was also shown that with the cloud test there is need of a bath to prevent the overcooling of the sides of the tube.

The work of the year has been very valuable, and it seems probable that in another year a method can be devised which will give satisfaction.

REPORT ON DAIRY PRODUCTS.

By Albert E. Leach, *Referee.*

During the past year a large number of samples of milk have been examined in the laboratory of food and drug inspection of the Massachusetts State board of health by the provisional method for the detection of added water from a refractometric examination of the milk serum. The method has been of great service in routine work for distinguishing between milk to which water has been fraudulently added and milk that simply is below the legal standard as it comes from the cow.

In view of the fact that according to law $50 is the minimum fine in Massachusetts, if the milk can be proved in court to be actually watered, while the fine for milk simply below the standard may be as low as the judge sees fit to impose, the importance of being able to distinguish between the two classes and to prove the presence of added

water is evident. More than 40 court cases have been tried in our State courts during the past year in which the complaint for added water was based on the provisional refractometric method, and in at least 95 per cent of these cases conviction was secured.

The accompanying chart has been prepared to show graphically the results of the determination of solids not fat and of the refraction of the serum of 141 samples of milk all below 12 per cent in total solids. The lower curves show the variation from sample to sample in the percentage of solids not fat, while the upper curves show the refraction of the milk serum in the same samples. The samples are arranged in the order of the solids not fat, the refractometric reading corresponding to the solids not fat in each sample being readily apparent as it is placed along the same ordinate in the chart.

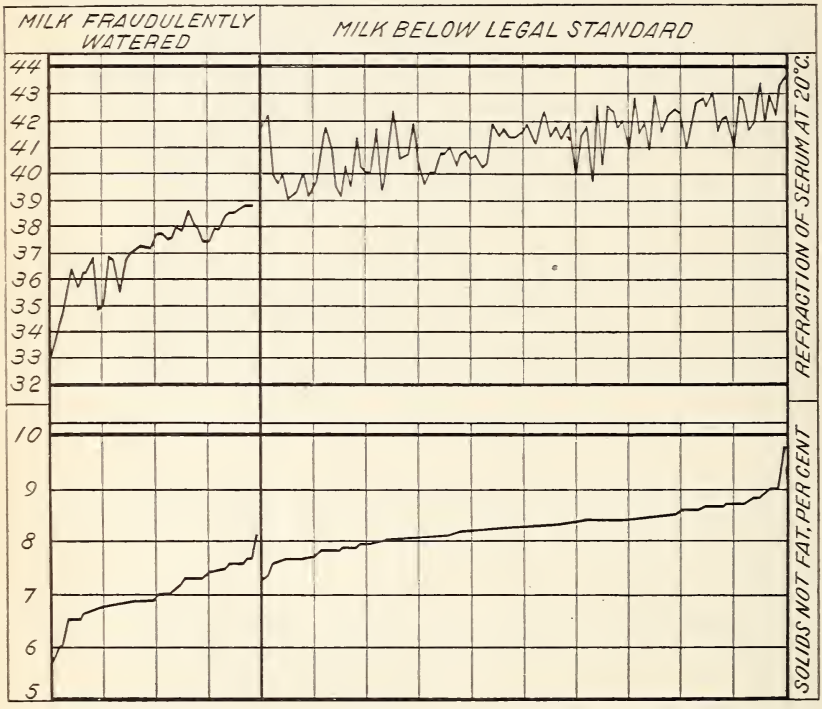

FIG. 1.—Comparison of refractometric examination of milk serum and the determination of solids not fat for detection of added water.

The first 40 samples of milk were pronounced fraudulently watered, since all stand in refraction of serum below 39°, as shown by the upper curve. The rest of these samples, even though they all were below the legal standard of total solids, can not be declared fraudulently watered.

If we were to determine the watered samples from the solids not fat alone, assuming 7.3 as the minimum solids not fat for a pure milk, we could only condemn 29 of the samples as being fraudulently watered, thus allowing at least 11 samples to escape detection. It is also apparent from a comparison of the two curves that there is no fixed proportion between the solids not fat and the refraction of the serum, since in some cases a milk low in one constant is found to be high in the other.

REPORT ON CONDIMENTS OTHER THAN SPICES.

By R. E. Doolittle, *Associate Referee.*

In presenting the report on condiments other than spices there is but little to offer in the way of original investigations. The referee, finding that no methods for the examination of this class of products had ever been presented to the association, has outlined certain methods which in his experience are of value in judging the character and purity of products coming under this subdivision. These methods are not restricted to products of this class but are, at least for the most part, methods applicable to other products, especially those closely allied to condiments other than spices. In fact, this subdivision overlaps some of the other subjects for which methods have already been adopted provisionally. In this classification, therefore, only such products have been included as are not generally included under any of the other subdivisions.

The referee recommends that these methods be adopted provisionally but that in the printing of the same they be given by reference wherever such methods appear under other subjects.

Methods for the Analysis of Condiments other than Spices.

(1) general discussion.

Under this head are included those mixed and prepared products used for the purpose of seasoning or giving relish to food. The various table sauces, catchups, horseradish, chutneys, and soys may be enumerated as examples of the principal products designated by this term. These preparations often vary widely in composition, as a various number of substances are used in their manufacture according to recipes that have been found to produce a characteristic flavor or pungency. In the examination of these products it may be assumed that no substance should be present that has no value as a food or flavoring material. Inert substances, known commercially as fillers, should be regarded as adulterants. Preservatives and coloring matters are the other adulterants most commonly present.

(2) microscopic examination.

Submit all samples containing solid substances to a microscopic examination for identification of these ingredients.

(3) preparation of sample.

Insure a uniform mixture by thorough stirring or shaking. Products containing solid substances should be reduced to a pulp by passing through a food chopper or grinding in a mortar.

(4) determination of solids.

Weigh 5 grams of the substance into a large flat-bottomed platinum dish, evaporate on steam bath to apparent dryness and then in oven at 100° C. to constant weight.

(5) determination of ash.

Thoroughly char the residue from determination of total solids at as low a heat as possible, extract with hot water, filter, and wash. Return the filter paper holding the insoluble matter to the dish and thoroughly ignite; add the soluble portion, evaporate to dryness, and ignite carefully at low redness. Cool in desiccator and weigh.

(6) DETERMINATION OF CHLORIN.

Dissolve the ash in hot water, cool, and dilute to 250 cc. Titrate 50 cc of solution with tenth-normal silver nitrate, using potassium chromate as indicator.[a]

(7) DETERMINATION OF TOTAL ACIDITY.

Dilute 5 grams of the material to 500 cc, thoroughly mix and titrate 100 cc of the diluted solution with tenth-normal sodium hydroxid, using phenolphthalein as indicator.

(8) DETERMINATION OF VOLATILE ACIDS.

To 10 grams of the material add 50 cc of water and distil in a current of steam until 250 cc pass over. Titrate the distillate with tenth-normal sodium hydroxid, using phenolphthalein as indicator.

(9) DETERMINATION OF NITROGEN.

Determine nitrogen on 5-gram sample by Kjeldahl method.[b]

(10) POLARIZATION.

Dilute 26.048 grams of the sample to about 150 cc in a 200 cc sugar flask, add an excess of lead subacetate, make to mark, thoroughly mix, filter, and polarize in a 200 mm tube, observing the temperature at which the reading is made. Invert 50 cc of the filtrate in a 100 cc sugar flask, using 5 cc of hydrochloric acid and heating to 68 C. in 15 minutes, nearly neutralize with dilute sodium hydroxid, cool, make to mark, and polarize in 200 mm tube. Correct to normal weight by multiplying the direct reading by 2 and the invert reading by 4. Both readings should be made at or near 20° C.

Determination of cane sugar.

(*a*) FROM POLARIZATION.

From the direct and invert readings calculate the cane sugar by the modified Clerget's formula,

$$S=\frac{100\ (a-b)}{142.66-\frac{t}{2}}$$

(*b*) FROM INCREASE IN REDUCING SUGARS.

When only small percentages of cane sugar are present it may be best determined from the increase in reducing sugars after inversion. The increase in per cent multiplied by 0.95 equals percentage of cane sugar.

(11) DETERMINATION OF REDUCING SUGARS BEFORE INVERSION.

Transfer 10 cc of solution prepared for direct polarization to a 250 cc flask; add sufficient sodium sulphate to precipitate excess of lead, make to mark, mix, and filter through a dry filter. Determine reducing sugars by official methods for determination of invert sugar.[c]

(12) DETERMINATION OF REDUCING SUGARS AFTER INVERSION.

Transfer 5 cc of invert solution prepared for polarization to a 250 cc flask, make to mark, and determine reducing sugars by official method for determination of invert sugar.[c]

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[a] Sutton's Volumetric Analysis, 9th edition, page 42.

[b] U. S. Dept. of Agr., Bureau of Chemistry, Bul. 46, p. 14.

[c] Ibid., p. 33.

(13) DETERMINATION OF HEAVY METALS.

Proceed as directed under "VII. Canned vegetables," Bulletin 65, page 53, 10 (b).

(14) DETECTION OF COLORING MATTER.

Proceed as directed under "XVII. Coloring matter," Bulletin 65, page 111.

(15) DETECTION OF PRESERVATIVES.

Proceed as directed under "Food Preservatives," Circular 28.

REPORT ON TEA AND COFFEE.

By C. D. HOWARD, *Associate Referee.*

INTRODUCTION.

The time available for this study has been unexpectedly limited this year, no cooperative work having been attempted, and as far as the improvement of methods is concerned the results attained have been largely negative. The work has been confined principally to a study of methods for the estimation of caffetannic acid.

Of late a number of brands of coffee have made their appearance concerning which the claim is made that the "tannin" has been removed. The following analyses, made at the New Hampshire laboratory of hygiene, show the relative composition of three of these so-called tanninless coffees, also of ordinary coffee and of coffee chaff:

Comparison of analyses of tanninless coffees, coffee, and coffee chaff.

Sample.	Water.	Ash.	Fat.	Fiber.	Caffeine.	Caffetannic acid (Krug's method).
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
No. 1 Tanninless coffees	2.70	4.10	13.18	18.46	1.17	10.76
No. 2 Tanninless coffees	2.70	4.05	14.12	15.70	1.33	11.04
No. 3 Tanninless coffees	2.26	3.61	12.55	22.70	.87	7.61
Java and Mocha	3.13	4.13	14.10	15.50	1.29	11.17
Coffee chaff	2.60	5.65	9.30	26.50	.40	5.98

In two of these cases the manufacturers base their claim for the "complete removal of tannic acid" upon the elimination, during the process of grinding, of the chaff or skin occurring on the surface and, to some extent, enmeshed in the groove of the coffee bean. The fallacy of such a claim, however, is evident from the composition of the chaff. Sample No. 3 represents a coffee of a different type, the claim being that by certain extractive processes "all of the tannin and caffeine" have been removed. As there are now several processes of this nature and as the popular demand for "hygienic" foods is likely to add to the number of brands of such products now upon the market, the desirability of accurate and fairly rapid methods for the estimation of caffetannic acid and caffeine is obvious.

CAFFETANNIC ACID.

CONSTITUTION.

The exact constitution of caffetannic acid still seems to be a matter of some doubt. Allen (Commercial Organic Analysis) gives the empirical formula as $C_{14}H_{16}O_7$; in Smith's translation of Richter's Organic Chemistry it is represented as $C_{30}H_{18}O_{16}$, while Krug bases a factor on the formula advanced by Hlasiwetz,[a] viz, $C_{15}H_{18}O_8$.

[a] Ann. Chem. Pharm., 1867, *142*: 230.

The later investigations of Cazeneuve and Haddon,[a] represent this body as being a diglucoside of dioxycinammic acid,[b] having the composition $C_6H_3\begin{cases}CH{=}CH.\,COOH\\O.\,C_6H_{11}O_5\\O.\,C_6H_{11}O_5\end{cases}$

They find that the acid gives a crystalline osazone of yellow needles melting at 180°, very slightly soluble in alcohol, of the following composition:

$$C_6H_3\begin{cases}CH{=}CH.\,COOH\\O.\,C_6H_9O_3(N{-}NH.\,C_6H_5)_2\\O.\,C_6H_9O_3(N{-}NH.\,C_6H_5)_2\end{cases}$$

While it would seem that the Cazeneuve and Haddon formula—indicating a di- rather than a mono-glucoside—is probably correct, yet so far as can be learned it has not as yet been verified by other investigators; unfortunately no time was available for any study in this connection.

The form of combination in which caffetannic acid exists naturally has not as yet been definitely established. Bell (Chemistry of Foods) designates it as a "chlorogenate (caffetannate) of potash and caffeine." This view is probably based upon the work of Payen [c] published in 1849. Allen (Commercial Organic Analysis) states that caffetannic acid occurs "probably as a calcium of magnesium salt." That the latter form of combination, or one similar, is the true one would seem to be indicated in some degree by the comparatively recent investigations of Trillich and Göckel [d] in connection with a proposed method for the estimation of this body based upon extraction with ether and benzol in the presence of an acid.

As prepared by precipitating an alcoholic infusion of coffee with lead acetate, filtering, and decomposing the lead precipitate with hydrogen sulphid, caffetannic acid forms a brownish sirup-like mass, having a slightly acid and astringent taste. The lead salt on drying becomes hard and brittle and is apparently somewhat hygroscopic.

BEHAVIOR TOWARD REAGENTS.

On boiling caffetannic acid with dilute acids, glucose and caffeic acid (di-oxycinammic acid) are formed. Caffeic acid also results on heating the solution with caustic alkali. Fusion with caustic potash yields pyrocatechuic and acetic acids. Caffetannic acid precipitates solution of gelatin but slightly, and this only in the presence of a large excess of the reagent, thus affording a marked contrast with the behavior of tea tannin.

Iron alum gives a greenish black precipitate or color; bromin and iodin give light, finely flocculent precipitates of a yellowish color. Copper acetate affords a greenish precipitate, filtered with difficulty; ammoniacal copper-sulphate solution a bulky precipitate, the greater part of which is easily soluble in a slight excess of ammonia.

Lead acetate yields a voluminous precipitate, calcium and barium hydroxids slighter ones; the latter tend to become slimy on the filter and wash with difficulty. An ammoniacal solution of potassium ferricyanid fails to produce the characteristic blood-red color afforded by dilute solutions of the ordinary tannins, the tint produced being dull brownish red. The volumetric procedure of Fletcher and Allen employed for estimating the tannin of tea by precipitation with standard lead acetate solution is therefore not applicable to coffee.

Unlike that of tea, the tannin of coffee gives no precipitate whatever with neutral or ammoniacal zinc solutions. Certain alkaloidal salts (quinin and cinchonin especially)

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[a] Comptes Rendus, 1897, *124*:1458.

[b] See also the work of Kunz-Krause, Ber. d. chem. Ges., 1897, *30*: 1617.

[c] Ann. chim. Phys. (3) *16*: 108.

[d] Zts. Nahr. Genussm., 1898, p. 101.

produce a somewhat erratic precipitation of caffetannic acid, but although some experiments were made using various indicators, this fact does not seem to be applicable as a basis for a quantitative method.

SOLUBILITY OF LEAD CAFFETANNATE.

In view of the fact that four of the five methods described below for the estimation of caffetannic acid involve precipitation as the lead salt, the following facts were determined relative to the solubility of this compound:

An infusion of roasted coffee, prepared by boiling with distilled water, exhibits a slightly acid reaction. If to such a hot infusion a perfectly neutral solution of lead acetate be added, the acidity of the filtrate from the resulting lead caffetannate will be found to be appreciably increased. Because lead caffetannate is slightly soluble in hot dilute acids it is therefore evident that precipitation by neutral lead acetate can never be quite complete, although if proper precaution be taken it is probable that the loss from this cause is inappreciable. Hot, moderately strong acid dissolves lead caffetannate completely. This salt is also very appreciably soluble in a large excess of neutral lead acetate. If basic lead acetate (avoiding excess) be employed as the precipitant, the resulting filtrate will be found to give no reaction for tannins with ferric acetate.

Lead caffetannate is slightly soluble in boiling distilled water, and in boiling 10 per cent alcohol. The perfectly clear filtrate obtained from boiling with 20 per cent alcohol gives no reaction for tannins with ferric acetate. With the use of stronger alcohol, however, a clear filtrate is more readily obtainable.

METHODS OF ESTIMATION.

Various methods for the quantitative determination of caffetannic acid have been proposed, no two of which give the same results, and all of which are in some degree fallacious. The chief difficulty has been in the fact that the true nature of this body has not until recently been understood, and that even now its exact constitution is not proven beyond question. In the past at least one method has been applied to some extent, based upon the assumption that tea tannin and coffee tannin gave similar reactions.

Bell's, or Payen's Method.

Five grams of coffee are exhausted with alcohol. The alcohol is evaporated and to the aqueous residue subacetate of lead is added. The precipitate is thrown on a filter, washed, decomposed with sulphuretted hydrogen. The filtrate from the plumbic sulphid is evaporated to dryness, when the caffetannic acid is obtained as a yellowish brittle mass.

By this method Trillich and Göckel found 5.32 and 3 per cent, respectively, of caffetannic acid in raw and unroasted coffee. Two serious defects in the above method, pointed out by Trillich and Göckel, are that every evaporation of the caffetannic acid extract results in a considerable proportion of the latter acid being rendered insoluble, and also that it is impossible by the ordinary procedure to completely decompose the lead precipitate with sulphuretted hydrogen on account of the tendency to occlusion of masses of this precipitate by the lead sulphid.

Proctor's Modification of Löwenthal's Method.

This method, official for estimating the tannin of tea, has also been applied to some extent in the case of coffee, more especially for the sake of obtaining comparative values on different brands. That the results obtained possess only relative values is evident from the behavior of coffee extract with gelatin, and also because of the fact that the ordinary tannic acid values for the permanganate solution have no application in this case.

Through the courtesy of a Boston coffee house data obtained in 1906 by the analyses of twenty samples of roasted coffee were made available. The average percentage of tannin, estimated by the Löwenthal process, was found to be 4.63.

Krug's Method.

Treat 2 grams of the coffee with 10 cc of water and digest for 36 hours; add 25 cc of 90 per cent alcohol and digest 24 hours more; filter, and wash with 90 per cent alcohol. The filtrate contains tannin, caffein, color, and fat. Heat the filtrate to the boiling point and add a saturated solution of lead acetate. If this is carefully done, a caffetannate of lead will be precipitated containing 49 per cent of lead. As soon as the precipitate has become flocculent, collect on a tared filter, wash with 90 per cent alcohol until free from lead, wash with ether, dry, and weigh. According to Krug the precipitate has the composition $Pb_3 (C_{15}H_{15} O_8)_2$. Weight of precipitate multiplied by 0.51597 gives the weight of caffetannic acid.

By this process Krug found 10.88 per cent of caffetannic acid in a sample of unroasted Java. Trillich and Göckel, working on an unroasted New Granada coffee, obtained the figures 11.12 and 11.50, while a roasted coffee of this variety gave 10.68 and 11.32 per cent. Results obtained by the writer using this method on roasted coffees varied from 10.65 to 11.17 per cent, duplicate determinations on a sample of Java and Mocha blend giving 10.65, 10.69, and 11.02 per cent. Some difficulty was experienced in securing a constant weight for the lead precipitate.

The principal objection to this method is its tediousness, the preliminary digestion consuming a large amount of time and the washing of the lead precipitate being a very slow and troublesome process.

Method of Trillich and Göckel.[a]

Boil 3 grams of coffee one-half hour with water, filter, and repeat this treatment on the residue three times. The united filtrates are made up to 1,000 cc. To 400 cc add 1 cc of basic lead acetate solution and allow to stand over night. Filter, wash, decompose the precipitate with sulphuretted hydrogen, filter from lead sulphid, evaporate to dryness and weigh.

Trillich and Göckel obtained by this method 10.88 and 11.37 per cent on raw and 7.99 and 8.60 per cent on roasted coffee. These authors also attempted to base a method upon extraction with ether in the presence of hydrochloric acid, but found that boiling with the latter acid occasioned some destruction of the tannin, while phosphoric acid did not appear to be capable of liberating caffetannic acid from the bases with which it is combined.

They conclude, as a result of their investigations, that the structure of caffetannic acid is not altered by the roasting process; also that all methods based upon precipitation with lead acetate are in some degree fallacious in that such precipitate appears not to consist wholly of caffetannate.

Hydrolytic method.

Some time was given to a study of a method involving hydrolysis of the glucosid by boiling with hydrochloric acid and subsequent estimation of the resulting glucose. Five grams of coffee were boiled one-half hour with 100 cc of water and the extract decanted through a filter. This treatment was repeated several times and the filtrates made up to 500 cc. From 200 to 400 cc, equivalent to 2 to 4 grams of coffee, were precipitated with lead acetate, the precipitate washed sufficiently to remove the small proportion of sugars present and then submitted to hydrolysis by heating in a water bath with hydrochloric acid. The reducing sugars were then estimated by Allihn's method.

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[a] Zts. Nahr. Genussm., 1898, p. 101.

In the following table the percentages of reducing sugars, considered as $C_6H_{12}O_6$, are calculated to caffetannic acid for both the mono- and di-glucosid formulas attributed to this body.

Estimations of caffetannic acid by the hydrolytic method using varying strengths of hydrochloric acid.

Strength of acid.	Time.	Cupric oxid in 0.5 gram.	Reducing sugars.	Caffetannic acid.	
				For C_{21}.	For C_{15}.
Per cent.	*Hours.*		*Per cent.*	*Per cent.*	*Per cent.*
2½	3	0.0480	4.02	5.63	7.28
2½	6	.0647	5.36	7.50	9.71
5	3	.0600	4.98	6.97	9.01
5	4	.0625	5.38	7.53	9.74
5	6	.0795	6.52	9.13	11.80
5	8	.0890	7.28	10.19	13.18
7½	3	.0840	6.88	9.63	12.45
7½	4	.0795	6.52	9.13	11.80
7½	5	.0770	6.32	8.85	11.44
7½	5	.0737	6.06	8.48	10.97
7½	6	.0790	6.48	9.07	11.73
7½	8	.0800	6.56	9.18	11.87
10	3	.0755	6.20	8.68	11.22
10	6	.0597	4.87	6.82	8.81

It is evident that this glucosid offers considerable resistance to decomposition. The strength of hydrochloric acid ordinarily employed for hydrolysis is insufficient, acid of between 5 and 10 per cent affording the maximum yield of sugar. Recognizing that the Krug method gives results necessarily somewhat too high, the above values would appear to point to the correctness of the Cazeneuve and Haddon formula, especially as under the conditions most favorable to complete hydrolysis (not yet ascertained), the proportion of caffetannic acid, assuming the formula $C_{15}H_{18}O_8$, would be materially in excess of that actually afforded by the Krug method.

This method is much less tedious than that of Krug, and has the advantage that the results obtained are directly referable to a definite formula for caffetannic acid. Not only are there differences of opinion as regards the composition of the lead salt, but it is certain that the percentage of lead in the latter varies with the conditions under which the precipitation is effected. On the other hand, the hydrolysis of the caffetannic acid, as carried out by the writer, proceeds somewhat erratically.

Recommendations.

It is recommended:

(1) That the methods here outlined for the estimation of caffetannic acid be submitted for cooperative study by the members of this association.

(2) That the Gomberg method for the determination of caffein be subjected to trial. This method can be logically carried out in connection with the caffetannic estimation, and is essentially as follows: The filtered extract, prepared by boiling the material with water, is precipitated by lead acetate and the precipitate filtered off and thoroughly washed with water. The excess of lead is removed from the filtrate by sulphuretted hydrogen and the latter expelled by boiling. An excess of a standard potassium iodid solution of iodin is added, the precipitate of the alkaloid with iodin filtered out, and the remaining iodin estimated by titration with sodium thiosulphate.

REVIEW OF METHODS FOR ANALYSIS OF TEA.

By R. E. Doolittle and F. O. Woodruff.

The authors being called upon during the past year to examine a number of samples of tea, have had occasion to study some of the many methods given in the literature for the chemical analysis of this product. As the results of these studies may be of use to the referee on the subject of tea, the following report is submitted.

The samples used in these investigations were the standards of 1905–6 employed by the Treasury Department for the examination of imported teas, and were of the following varieties:

Varieties of tea examined.

Variety.	Laboratory No.	Variety.	Laboratory No.
Oolong	1	Country green	7
Foochow oolong	2	Pan-fired Japan	8
North China congou	3	Basket-fired Japan	9
South China congou	4	Japan dust, or fannings	10
India	5	Capers	11
Ping Suey	6		

(1) Determination of Water Extract.

In the study of the methods for determination of water extract the method of Krauch, reported by the referee on tea and coffee at the twenty-first annual meeting of the association, was first considered.

Method of Krauch[a].—Treat 20 grams of the tea with 400 cc of water and heat on a boiling water bath for six hours. Filter through a tared filter, wash with water until the filtrate measures 1,000 cc dry, and weigh the residue. The water-soluble substance is determined by the difference.

The method as given is rather vague in some respects, and after some preliminary experiments the samples were run as follows:

Twenty grams of the tea were weighed into a liter flask. 400 cc of hot water added, the flask heated on steam bath for six hours, the volume of water being kept at 400 cc by addition of hot water from time to time. The contents of the flask were then filtered through a tared filter and washed with hot water until filtrate measured 1,000 cc. The residue was dried by transferring paper and contents to tared aluminium dish and heating to constant weight in steam oven.

The results obtained by this method were as follows:

Determination of water extract by the Krauch method, modified.

Laboratory No.	Per cent extracted in duplicate.		Laboratory No.	Per cent extracted in duplicate.	
1	32.26	40.56	7	30.44	[a]39.42
2	30.55	33.26	8	31.81	30.27
3	31.60	35.87	9	32.18	34.76
4	27.72	25.44	10	29.93	34.16
5	34.12	35.13	11	31.44	35.14
6	32.67	33.32			

[a] Triplicate, 39.87 per cent.

Several difficulties were encountered in the manipulation of the method, which was found to be long and tedious, requiring in some cases, with green teas, two days to secure the 1,000 cc of filtrate. The large amount of sample used made it almost impossible

[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 90, p. 38; König, Zts. Nahr. Genussm., 3d edition, p. 1057.

to dry the residue to constant weight, and the size of the filter paper required undoubtedly gave a large error from change in weight. It was not possible to completely extract so great a quantity of tea with the volume of water used. Duplicate determinations did not check sufficiently close.

As it was found that the principal difficulties in the manipulation of the Krauch method arose from the large quantity of sample used for the determination, it was decided to try smaller quantities. From our own experiments and a review of the methods given in the literature 2 grams was decided upon as a sufficient quantity for extraction.

To determine the length of time necessary to secure complete extraction of the 2 grams of tea, sample No. 1 was extracted by boiling with 200 cc of water for various lengths of time, washing the residues until the total filtrate measured 500 cc. Results obtained were as follows:

Results obtained by varying the time of extraction.

Time.	Per cent extracted.	Time.	Per cent extracted.	Time.	Per cent extracted.
Minutes.		*Minutes.*		*Minutes.*	
5.....	42.47	25.....	44.53	45.....	44.78
10.....	42.51	30.....	43.82	50.....	44.54
15.....	43.32	35.....	43.91	55.....	[a] 45.62
20.....	44.21	40.....	44.06	60.....	[b] 45.67

[a] Duplicate, 45.87 per cent.
[b] Duplicate, 45.07; triplicate, 46.50 per cent.

To determine the volume of water required for extraction, 2-gram samples of No. 1 were boiled for 30 minutes with varying amounts of water, all being filtered and washed with hot water until filtrate measured 500 cc. Results were as follows:

Results obtained by varying the amounts of water used.

Water used.	Per cent extracted.	Water used.	Per cent extracted.
cc.		cc.	
100	44.47	200	44.10
125	43.82	250	44.50
150	43.81	300	44.10
175	44.54		

The matter of weighing the residue was considered, whether or not it is advisable to weigh separately or with the filter paper. Duplicate samples were run, weighing the residues in the first instance with filter by means of a weighing bottle, and in the second by removing the residue to a tared dish and weighing separately. Results were as follows:

Two methods of weighing residue compared.

Laboratory No.	Amount extracted.		Laboratory No.	Amount extracted.	
	Residue and paper with adhering particles separately determined.	Residue and paper weighed together in weighing bottle.		Residue and paper with adhering particles separately determined.	Residue and paper weighed together in weighing bottle.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
1	[a] 41.65	[b] 44.16	7	[c] 39.87	[d] 40.16
2	42.01	43.05	8	38.12	41.13
3	38.71	36.71	9	41.24	41.27
4	46.35	38.62	10	.....	.....
5	44.62	44.92	11	.....	43.67
6	36.97	.....			

[a] Duplicate, 41.71; triplicate, 41.51.
[b] Duplicate, 43.82.
[c] Duplicate, 41.47; triplicate, 39.42.
[d] Duplicate, 41.25.

As a result of these studies the following method is suggested for the determination of extract in tea:

To 2 grams of the tea in a 500 cc Erlenmeyer flask add 200 cc of hot water and boil with low flame for one hour. The flask should be closed with a rubber stopper through which passes a glass tube 18 inches long for condenser. The loss from evaporation should also be replaced from time to time by addition of hot water. Filter through a tared filter and wash the residue until the filtrate measures 500 cc, stirring the contents of the filter throughout the process to facilitate the filtering. Reserve filtrate and washings for determination of tannin and theine. Dry the filter paper and residue in its funnel in the steam oven until the excess of water is removed, transfer paper and contents to tared weighing bottle and dry to constant weight at 100° C.

(2) Determination of Tannin.

Tannin was determined on the eleven samples by the Proctor modification of Löwenthal's method [a] with the following results:

Tannin determinations (Proctor-Löwenthal method).

Laboratory No.	Per cent of tannin found in duplicate.		Laboratory No.	Per cent of tannin found in duplicate.	
1	8.42	7.89	7	8.42	5.33
2	9.62	9.45	8	6.69	7.21
3	6.61	6.36	9	7.04	6.87
4	7.56	.....	10	6.36	8.58
5	8.76	9.27	11	9.27	.....
6	7.39	5.33			

To avoid the necessity of making a separate infusion for the determination of tannin the experiment was made of using an aliquot portion of the filtrate from the determination of water extract. The determination was made as follows:

The filtrate from the determination of water extract was made to 500 cc. To 25 cc of this volume 25 cc of indigo carmine solution and about 750 cc of water were added and the whole titrated with standard permanganate solution. Two hundred and fifty cc of the solution was next mixed with 50 cc of gelatin solution, 100 cc of salt solution, and 10 grams of kaolin added and the whole shaken for five minutes. This was decanted through a filter. To 40 cc of the filtrate 25 cc of the indigo carmine solution and 750 cc of water were added and titrated as before.

[a] U. S. Dept. Agr., Bureau of Chemistry Bul. 90, p. 39.

The following results were obtained, which for the purpose of comparison are here tabulated with the results obtained by the Proctor modification of Löwenthal's method:

Comparison of tannin results by the Proctor modification of the Löwenthal method and the author's modification.

Laboratory No.	Per cent of tannin.		Laboratory No.	Per cent of tannin.	
	Experimental method.	Löwenthal method.		Experimental method.	Löwenthal method.
1	8.76	8.42	7	6.52	8.42
3	6.76	6.61	9	9.00	7.04
4	7.44	7.56	10	6.92	6.36
5	9.18	8.76	11	9.52	9.27
6	7.76	7.39			

To further check the methods, duplicate determinations were made on two samples. Results obtained were as follows:

(*a*) First determination, 8.07 per cent; duplicate, 8.42 per cent. (*b*) First determination, 8.76 per cent; duplicate, 8.93 per cent. Corresponding to a difference in titration of 0.2 cc and 0.1 cc, respectively.

The results being as satisfactory when the filtrate from the determination of water extract was used, which is a saving of much time, the authors would suggest the following modification in manipulation of the Löwenthal method: [a]

Cool and make to 500 cc the filtrate from the determination of water extract. To 25 cc add 25 cc indigo carmine solution and about 750 cc water, and titrate with standard permanganate solution, beginning with 1 drop at a time for 20 drops, then 1 cc at a time till color is a light green, then very carefully until a faint pink appears around edge of fluid. Number of cubic centimeters used = *a*.

Mix 250 cc clear filtrate with 50 cc gelatin solution, 100 cc salt solution, cork, add 10 grams kaolin, and shake five minutes; decant, then filter. To 40 cc of the filtrate add 25 cc indigo solution, 750 cc water, and titrate as above. Number of cubic centimeters of permanganate used= *b*. a — *b* = *c* = permanganate ($KMnO_4$) required to oxidize the tannin; 0.04157 gram of tannin = 0.063 gram of oxalic acid.

(3) Determination of Theine.

Theine was determined on one sample of tea by the following methods with the following results:

Determinations of theine by different methods.

Method.	Per cent of theine in duplicate.	
Dvorkowitsch [a]	2.56	2.41
Stahlschmidt [b]	2.38	2.28
Commaille [c]	1.51	.....

[a] Bureau of Chemistry Bulletin 90, p. 39; also König, Zts. Nahr. Genussm., 4th ed., p. 1010.
[b] Leach, Food Inspection Analysis, p. 281.
[c] Blyth, Foods: Their Composition and Analysis, 5th ed., p. 334.

The experiment was then made of determining the theine by the Dvorkowitsch method on an aliquot portion of filtrate from water extract determination. A determination on the same sample (No. 4) as was used for the above determinations gave 2.62 per cent of theine. The samples run by this modification gave the following results:

[a] For reagents and standard solutions see Bureau of Chemistry Bulletin 90, p. 39.

Determinations of theine by a modification of the Dvorkowitsch method.

Laboratory No.	Theine.	Melting point of crystals.	Laboratory No.	Theine.	Melting point of crystals.
	Per cent.	° *C.*		*Per cent.*	° *C.*
1	2.874	226	7	2.070	232
2	2.396	229	8	1.994	231
3	2.542	234	9	2.032	228
4	2.620	231	10	1.356	233
5	3.270	228	11	1.898	231
6	1.716	.....			

The authors would suggest the following modification of the Dvorkowitsch method for determination of theine:

Extract 225 cc of the filtrate obtained from determination of water extract made to 500 cc in a separatory funnel with petrolic ether to remove fat. To the fat-free portion add 50 cc of a 4 per cent barium hydrate solution, shake well, and filter. To the filtrate add 50 cc of a 20 per cent sodium chlorid solution and extract four times with 75 cc portions of chloroform, distil off most of the chloroform from the four combined portions, and evaporate the remainder in a weighed platinum dish, dry at temperature of steam oven to constant weight.

(4) Determination of Moisture.

The method usually given for the determination of moisture in tea is to dry 2 to 5 grams of the sample in a flat-bottomed dish at 100° C. Doolittle and Ogden determined the loss of weight in a number of samples of tea by drying in an oven at temperature of boiling water and by drying in a current of hydrogen[a] at temperature of boiling water. The following results were obtained:

Comparisons of different methods of drying.

Laboratory No.	Variety of tea.	Loss in oven at temperature of boiling water.	Loss in air oven at 110°.	Loss in current of hydrogen.
	U. S. standards 1905–6.	*Per cent.*	*Per cent.*	*Per cent.*
1	Formosa	5.84	6.50	7.68
2	Foochow oolong	6.09	6.49	7.52
3	North China congou	7.58	8.68	9.25
4	South China congou	7.55	.....	9.26
5	India	5.57	6.50	7.75
6	Ping Suey	5.31	6.18	6.73
7	Country green	5.79	7.45	7.75
8	Pan-fired Japan	5.00	6.02	6.72
9	Basket-fired Japan	5.20	6.26	6.70
10	Japan dust or fannings	5.68	6.77	7.57
11	Capers	6.71	7.16	8.36
	Commercial.			
12	Formósa oolong	5.41	6.48	7.39
13	Foochow oolong	6.04	6.52	7.38
14	Congou	7.12	7.84	9.47
15	India	.....	.....	7.43
16	Ping Suey	5.40	6.04	7.61
17	Country green	5.82	6.87	.....
18	Pan-fired Japan	3.59	4.54	5.09
19	Basket-fired Japan	5.77	6.74	7.61
20	Japan siftings	5.96	7.00	7.73

[a] For description of hydrogen drying oven used see Ann. Rept. Conn. Agr. Exp. Sta., 1889, p. 187.

REPORT ON FOOD PRESERVATIVES.

By W. L. Dubois, *Associate Referee.*

During the past year the referee has confined his attention almost entirely to the quantitative estimation of salicylic acid. A method was first worked out for the estimation of a water solution of salicylic acid and attempts were then made to apply this method to various food products.

Salicylic Acid in Water.

GENERAL METHOD.

For this determination ether was selected as the solvent and experiments made to prescribe certain details of manipulation. The following points were determined:

(1) Four successive extractions with ether remove all but a trace of salicylic acid.

(2) Washing the combined ether solutions twice with 25 cc of water removes all the mineral acid and only a trace of the preservative. A smaller amount of water is not so satisfactory.

(3) The use of more than a small amount of alcohol in dissolving salicylic acid previous to diluting to volume is inadvisable because the color reaction is inhibited thereby. Warm water is a more satisfactory solvent than dilute alcohol for this reason. (See Table 8.)

(4) For the most satisfactory matching of colors it is advisable to have the strength of the standard and that of the solution to be compared therewith approximately the same. One milligram of salicylic acid in 50 cc is a very convenient amount. It is also well to keep the temperature of both the standard and the solution approximately the same.

(5) For producing the color a 2 per cent solution of ferric alum, boiled for a minute or two and filtered, is very satisfactory. This solution does not cause cloudiness when used for the test, and an excess of 1 cc does not influence the delicacy of the reaction.

Three water solutions of sodium salicylate were sent out to determine the most convenient quantity of ether to use at each extraction, and to learn whether any loss of salicylic acid resulted from distilling the ether. From the results obtained (as shown in Table 1) it does not appear that distilling the ether causes loss of salicylic acid, nor does the use of the larger quantity of ether insure a more complete extraction. In the opinion of the referee it is safer to evaporate the ether solution until about 20 cc remain, allowing this last portion to volatilize spontaneously. With this modification the method is satisfactory for water solutions of salicylic acid.

TABLE 1.—*Determination of salicylic acid in water solution.*

Analyst.	Sample No.	Salicylic acid added.	Salicylic acid recovered.			
			50 cc ether, at each extraction, distilled—	75 cc ether, at each extraction, distilled—	50 cc ether, at each extraction, evaporated spontaneously—	75 cc ether, at each extraction, evaporated spontaneously—
		mgs.	*mgs.*	*mgs.*	*mgs.*	*mgs.*
B. H. Smith	1	10	8.0	8.5	9.0	9.5
	2	30	25.0	24.0	26.0	27.5
	3	50	45.0	45.0	48.0	48.0
W. S. Richardson	1	10	6.0	4.5	8.0	10.0
	2	30	25.0	25.0	25.0	25.0
	3	50	50.0	50.0	50.0	50.0
F. O. Woodruff	1	10	9.2	8.4	8.0	9.4
	2	30	28.0	28.5	28.5	21.0
	3	50	46.3	43.8	41.3	41.3
C. W. Harrison	1	10	5.6	5.25	4.6	5.5
	2	30	24.0	.....	24.0	22.8
	3	50	45.0	48.0	45.0	47.5
W. L. Dubois	1	10	10.0	9.43	9.3	9.3
	2	30	29.1	30.50	30.5	30.5
	3	50	50.0	50.0	50.0	.....

SALICYLIC ACID IN BEER.

In applying this method to light beer the referee has found that if at each extraction a volume of ether at least equal to that of the beer extracted be used little trouble with emulsions is experienced and the determination is quite satisfactory. A small amount of coloring matter is found in the ether extract, but the quantity is not sufficient to cause any trouble. If after distilling all but the last 20 cc the beaker be allowed to stand over night or for a number of hours in a vacuum desiccator, the salicylic acid will usually crystallize and may be taken up directly in water. The following results were obtained by the referee:

TABLE 2.—*Determination of salicylic acid in beer.*

Sample.	Amount added to 100 cc.	Amount found.	Per cent recovered.	Sample.	Amount added to 100 cc.	Amount found.	Per cent recovered.
	mgs.	*mgs.*			*mgs.*	*mgs.*	
A	10	8.0	80.0	E	30	25.0	83.3
B	25	22.4	90.0	F	40	36.4	90.9
C	10	8.7	87.0	G	50	40.0	80.0
D	20	17.9	89.3				

SALICYLIC ACID IN WINE.

MODIFICATION OF GENERAL METHOD.

When applied to wine, either white or red, this method does not give results that are at all satisfactory. The amount of interfering ether extractive is such as to prohibit taking up directly in water. To avoid this difficulty, a common practice heretofore has been to exhaust the dried ether extract with low boiling-point gasolene (boiling point 40°–50° C.), but we have found that in many cases this solvent extracts only a small per cent of the salicylic acid present.

In Table 3 are given a few results obtained by extracting four times with ether and exhausting the dried extract with a low boiling-point gasolene.

TABLE 3.—*Determination of salicylic acid in wine.*

Analyst.	Amounts of salicylic acid recovered.			
	16389.	16390.	16391.	16392.
	mgs.	*mgs.*	*mgs.*	*mgs.*
H. V. Frost	0.000	0.000	0.000	0.000
F. O. Woodruff	.075	.150	.100	.200
Edmund Clark	.027	.0536	.0803	.105
A. W. Ogden	.031	.014	.031	.016
B. H. Smith	Trace.	.133	.025	.060
C. W. Harrison	Trace.	Trace.	Trace.	Trace.
C. N. Berkeley	Trace.	Trace.	Trace.	Trace.
W. L. Dubois	.500	2.000	.700	1.500
Amount of salicylic acid added per 100 cc	5.000	20.000	7.500	17.500

The difficulty in the determination of salicylic acid in wine is due to those substances which are extracted by ether and interfere with the color reaction. A number of possible ways of avoiding this trouble have occurred to the referee:

(1) Find a solvent for salicylic acid which will dissolve it from the dried extract and leave behind other substances.

(2) Sublime salicylic acid from the dried ether extract.

(3) Precipitate out of solution, before extraction with ether, those bodies which interfere with the color reaction.

(4) Separate salicylic acid from wine with a solvent which will not extract interfering substances or by distillation with steam. (Not subjected to experiment.)

(5) Precipitate the salicylic acid from the solution instead of extracting. (Not subjected to experiment.)

1. VARIOUS SOLVENTS.

For taking up salicylic acid from the extract gasolene has been proved useless for quantitative work. In trying several other solvents 100 cc of wine were extracted with ether and salicylic acid added to the extract. The extract was then rubbed up with ten 5-cc portions of the solvents in question. The following results were obtained.

TABLE 4.—*Determination of salicylic acid in wine using different solvents.*

Solvent.	Salicylic acid present.	Salicylic acid recovered.	Per cent recovered.
	mgs.	*mgs.*	
Benzol	10	4	40
Carbon bisulphid	10	9.5	95
Carbon tetrachlorid	10	3.5	35
Gasolene (90 per cent) / Ether (10 per cent) [a]	10	5.2	52

[a] Larger percentages of ether seem to take up some coloring matter.

Wines containing known amounts of salicylic acid were extracted in the usual way with ether and the residue treated with ten 5-cc portions of carbon bisulphid. The results were as follows:

TABLE 5.—*Determination of salicylic acid in wine with ether extraction and carbon bisulphid.*

Wine.	Amount added.	Amount recovered.	Per cent recovered.	Wine.	Amount added.	Amount recovered.	Per cent recovered.
	mgs.	*mgs.*			*mgs.*	*mgs.*	
White	10	6.07	60.7	Red	10	7.9	79.0
Do	10	7.89	78.9	Do	20	15.0	75.0
Do	20	15.0	75.0	Do	20	17.64	88.2
Do	20	15.0	75.0				

Chloroform takes up too much coloring matter from the residue to be used for this purpose. For extracting the preservative from wine no satisfactory solvent was found which would not also dissolve interfering substances. Chloroform can be manipulated so as to extract but little tannin, but the referee has not been able to recover more than 50 per cent by four extractions with this solvent. Amyl alcohol produces such heavy emulsions that its use is not practicable. Mixtures of gasolene and ether in various proportions did not recover over 40 per cent in four extractions, nor were the extracts obtained free from coloring matter.

2. SUBLIMATION.

For subliming salicylic acid the referee tried the apparatus described by Bigelow (Bul. 90, p. 59), and also one made by substituting in the above a Trolius's nitrogen bulb for tube (b). It was found that the most satisfactory temperature for completely subliming salicylic acid is 185° to 195° C. Air should be drawn through at about three bubbles per second. Salicylic acid was dissolved from the collecting tube by dilute alcohol, diluted to a definite volume and an aliquot portion compared with a standard solution of salicylic acid. Under these conditions 90 to 100 per cent can be recovered when working with pure salicylic acid. When heating the extract from wine, however, an oily, colored substance frequently sublimes with the preservative and interferes with the color reaction. The referee obtained but indifferent results, sometimes recovering 80 per cent, but more frequently from 30 to 50 per cent.

3. TREATMENT OF WINE BEFORE EXTRACTION.

One hundred cubic centimeters of red wine containing 10 mg of salicylic acid were stirred up thoroughly with 2 grams of washed hide powder and filtered. The filtrate was extracted in the usual way with ether and 52 per cent of salicylic acid was recovered. One hundred cubic centimeters of wine containing 10 mg of salicylic acid were treated with gelatin solution and filtered. The filtrate was extracted in the usual way and 50 per cent was recovered.

One hundred cubic centimeters of red wine containing 10 mg of salicylic acid were made ammoniacal, ferric chlorid added, and the wine evaporated to 30 cc. The residue was transferred to a graduated flask, diluted to volume, and an aliquot portion filtered off. From this filtrate 4.8 mg of salicylic acid were recovered by extraction with ether.

Fifty cubic centimeters of red wine were saturated with zinc sulphate. The wine was not clarified by this process.

One hundred cubic centimeters of wine containing 10 mg of salicylic acid were treated with animal charcoal and filtered. Clarification was accomplished by this means, but the salicylic acid is also practically all removed.

Harry and Mummery's method.[a]—This method depends on the fact that lead tannate is insoluble in caustic alkali, while lead salicylate is soluble. In following the procedure for wine as laid down by these authors, the referee obtained the unsatisfactory results shown in Table 6. By experiment it was found that 5 cc of lead acetate were sufficient to precipitate all the tannin and coloring matter from 50 cc of wine. It was also found more satisfactory to add hydrochloric acid to the solution before diluting to volume and filtering, employing the method prescribed by these analysts for determining salicylic acid in jams, etc. The method as modified by the referee is as follows:

To 50 cc of wine, add 5 cc basic lead acetate, 30 cc of normal sodium hydroxid, and partially neutralize with 20 cc of normal hydrochloric acid. Dilute to 300 cc and filter 200 cc. Acidify with dilute hydrochloric acid and extract as directed for beer. The extract usually has some acetic acid in it, and this must be allowed to volatilize

[a] Analyst, 1905, *30*: 124.

before taking up the salicylic acid in water. Solution and comparison with standard is carried out as with beer. From red wines about 75 per cent of salicylic acid may be recovered. White wines, which would seem more easily handled, give only about 55 per cent, which fact remains unexplained.

TABLE 6.—*Salicylic acid in wine determined by Harry and Mummery's method.*

Wine.	Amount added.	Amount recovered.	Per cent recovered.	Wine.	Amount added.	Amount recovered.	Per cent recovered.
	mgs.	*mgs.*			*mgs.*	*mgs.*	
White	10	5.5	55	Red	10	6.6	66
Do	10	5.5	55	Do	10	7.5	75
Red	10	7.5	75	Do	10	6.8	68

SALICYLIC ACID IN TOMATOES, CATSUPS, ETC.

With this class of goods the material for analysis must receive some preliminary treatment to remove interfering extractives. In all the methods tried 50 grams pulped tomatoes were taken and the salicylic acid added.

METHOD 1.

Fifty grams of tomatoes were shaken 30 minutes with 150 cc of water made alkaline with sodium hydroxid. The mixture was centrifuged, the supernatant liquid poured through a filter, and an aliquot portion extracted with ether after acidifying. The residue remaining after evaporating the ether contained considerable coloring matter and other foreign substances and the method was abandoned.

METHOD 2.

Fifty grams of tomatoes and 100 cc of water were acidified with phosphoric acid and distilled with steam till 250 cc had passed over. The distillate was made alkaline, concentrated to 100 cc, acidified, and extracted with ether. No coloring matter or other foreign substances were present in the ether residue, but neither was salicylic acid in any quantity. No test was obtained with samples containing up to 100 mg per kilogram. In one having present 200 mg per kilogram, 0.5 mg was found, corresponding to 10 mg per kilogram.

For such samples, separation of salicylic acid by the above method is not quantitative. A very large volume of distillate is required to carry over any amount of salicylic acid, and that amount is only a small percentage of the preservative present. The method is not to be recommended if a better procedure be available.

METHOD 3.

Transfer 50 grams of pulped tomatoes to a 200 cc flask with 50 cc of water, and make alkaline with milk of lime. Complete to volume and filter as large an aliquot portion as possible. Usually 150 to 160 cc of filtrate may be obtained. Acidify with dilute hydrochloric acid and extract with ether four times, using from 75 to 100 cc of ether at each extraction. Wash the combined ether solution twice with 25 cc of water, and distil the ether slowly, allowing the last 20 to 25 cc to evaporate spontaneously. Take up the ether in dilute alcohol, make to a definite volume, using a few drops of a 2 per cent solution of ferric alum to produce the color. The results obtained by this method are shown in the following table:

TABLE 7.—*Determination of salicylic acid in tomatoes by Method 3.*

Sample.	Amount added.	Amount found.	Per cent recovered.	Sample.	Amount added.	Amount found.	Per cent recovered.
	mgs.	*mgs.*			*mgs.*	*mgs.*	
A	2.5	0.0	0.0	D	20.0	12.5	62.4
B	5.0	1.82	36.4	E	25.0	16.92	67.7
C	10.0	5.0	50.0	F	30.0	22.70	75.7

In the ether extract from sample A, crystals appearing to be salicylic acid were present, but no test for salicylic acid was obtained. This led to an investigation of the effect of alcohol on the color produced by ferric salts and salicylic acid and the following experiment was made:

A solution of 1 mg of salicylic acid in 50 cc of water, to which were added 3 drops of ferric solution, was used as a standard. The solutions matched against this contained 1 mg of salicylic acid and various quantities of alcohol in 50 cc, as shown in the table below:

TABLE 8.—*Effect of alcohol on color produced by ferric salts and salicylic acid.*

Alcohol in 50 cc.	Reading of standard.	Reading of solution examined.	Salicylic acid indicated in solution.	Remarks.
cc.			*mg.*	
5	20	20	1	
10	18	18	1	
15	18	18	1	Quality of color not the same.
20	20	21	.....	Color of sample decidedly bluer.
25	20	27	.....	Color quality identical.
30	20	37	.....	Do.
35	18	.....	.....	Color of sample too light to read.
40	18	.....	.....	Do.

It appears from these results that the presence of more than 10 cc of alcohol in the solution used is inadvisable. It is preferable to dissolve the ether extract in warm water, cool, and dilute to volume.

It is also an improvement to render the tomatoes alkaline with ammonia before adding the milk of lime. When this is done, about 15 cc milk of lime (200 grams of quicklime in 2,000 cc of water) are sufficient, whereas much more is necessary when the ammonia is not used. These two modifications in the method given above have solved the problem and give excellent results, as is shown by the following figures:

TABLE 9.—*Determination of salicylic acid in tomatoes by modified method.* (*Dubois.*)

Amount used.	Amount recovered.	Per cent recovered.	Amount used.	Amount recovered.	Per cent recovered.
mgs.	*mgs.*		*mgs.*	*mgs.*	
5	4.7	94.0	20	19.20	96.0
10	8.0	80.0	25	25.00	100.0
10	8.11	81.1	30	26.70	89.0
15	13.33	88.8	50	46.9	93.8

Two samples were sent out to the collaborators containing, respectively, 10 mg and 20 mg of salicylic acid in 50 grams of tomatoes, to be examined by the above method. The results obtained on these samples are given in the table below:

TABLE 10.—*Results obtained by collaborators on salicylic acid in tomatoes by modified method.*

Analyst.	No. 17073 (10 mg added).	No. 17074 (20 mg added).
C. S. Brinton	7.44	17.05
G. F. Mason	7.50	17.50
R. Hoagland	4.53	14.86
B. H. Smith	3.0	17.50

SALICYLIC ACID IN JAMS, MARMALADES, AND SIMILAR PRODUCTS.

The referee has found that Harry and Mummery's method is fairly satisfactory for this class of products, recovering from 60 to 75 per cent of the salicylic acid added. The method is as follows:

Fifty grams of the crushed sample to be tested are placed in a 300 cc flask with a small amount of water. Ten to 20 cc of a saturated solution of basic lead acetate are added and the whole made alkaline by the addition of 25 cc of roughly normal sodium hydroxid. Shake well and add from 15 to 20 cc of roughly normal hydrochloric acid. The contents of the flask are then diluted to the mark, well shaken, and an aliquot of 200 cc filtered off. This is acidified with hydrochloric acid and extracted with ether.

No comparative work has been done with other methods. In the table below are given a few results obtained by the referee:

TABLE 11.—*Determination of salicylic acid in jams, etc., by Harry and Mummery's method. (Dubois.)*

Amount added.	Amount recovered.	Per cent recovered.	Amount added.	Amount recovered.	Per cent recovered.
mgs.	*mgs.*		*mgs.*	*mgs.*	
10	6.42	64.2	30	15.00	50.0
10	6.17	61.7	10	6.17	61.7
20	15.00	75.0	25	14.06	56.3

RECOMMENDATIONS.

The referee recommends the following changes in Bulletin No. 65:

(1) Page 109, that the second method for the detection of benzoic acid be rewritten to read as follows:

Evaporate to dryness and treat the residue with 2 or 3 cc of concentrated sulphuric acid. Heat until white fumes appear. The organic matter is charred and benzoic acid is converted into sulpho-benzoic acid. A few crystals of ammonium or potassium nitrate are then added and the dish again heated until white fumes appear. Repeat this process until all organic matter is oxidized and the solution is practically colorless. This causes the formation of metadinitrobenzoic acid. When cool, the acid is diluted with an equal volume of water, ammonia added in excess, and the solution transferred to a test tube. This is cooled and a few drops of freshly prepared ammonium sulphid added in such a way that the solutions do not mix. The nitro compound becomes converted into ammonium metadinitrobenzoate which possesses a red color. This reaction takes place immediately and is seen at the surface of the liquid without stirring.

(2) Page 90, line 2, substitute "20 cc" for "5 cc." This change is considered advisable because when determining sulphurous acids in meat products about 20 cc of 20 per cent phosphoric acid is found to be necessary to completely evolve the sulphurous acid present. This amount would not be required for wines, but, as there

seems to be no objection to the use of the excess of phosphoric acid in this case, it is thought advisable to recommend a uniform quantity of phosphoric acid which will answer for all purposes.

(3) Page 90, after line 34, insert "Instead of titrating the excess of iodin with the standardized thiosulphate solution, the sulphurous acid distilled over may be determined directly by acidifying the iodin solution or an aliquot thereof with hydrochloric acid, boiling until colorless and precipitating sulphuric acid in the usual way with barium chlorid."

(4) Page 110, line 41, transpose the phrase "boiled to expel carbon dioxid" to line 40, inserting the same after the word "pink."

(5) Under method for boric acid insert the following method:

Weigh about 50 grams, make alkaline with milk of lime, evaporate to dryness and ash. Dissolve in hydrochloric acid, filter and wash. In case much carbon remains, burn the paper and residue after making alkaline with milk of lime and treat with hydrochloric acid as above. Make the filtrates alkaline with sodium hydroxid, boil, add barium hydroxid until no further precipitate is formed, and filter. Dissolve the precipitate in dilute hydrochloric acid and reprecipitate with sodium hydroxid with the addition of a few drops of barium hydroxid. Wash the precipitate with hot water, cool the filtrates and washings to room temperature, and dilute to definite volume. Take an aliquot portion, add methyl orange, and acidify. Boil to expel carbon dioxid, cool and add decinormal alkali until the pink color is just discharged. Add 5 or 6 grams of mannite and a few drops of phenolphthalein and titrate the boric acid, which is now all in the free state, with decinormal alkali. When the end point is obtained it is well to add more mannite to be sure that enough has been used.

(6) Eliminate from methods for salicylic acid directions to extract the residue with gasolene.

(7) Page 73, eliminate the resorcin method for formaldehyde, inasmuch as this method is unreliable and there are better ones available.

It is further recommended that the referee for the ensuing year conduct work along the following lines:

(1) Quantitative determination of salicylic acid in wines.

(2) Further experiments for the determination of salicylic acid in fruit products such as jams, marmalades, etc.

(3) Further trial of Harry and Mummery's method.

(4) Trial of method for the detection and determination of fluorids proposed by Woodman and Talbot (J. Amer. Chem. Soc., 1906, *28:* 1437).

The privileges of the Cosmos Club were extended to the convention through the secretary of the association, and the meeting adjourned until 2 o'clock.

WEDNESDAY—AFTERNOON SESSION.

REPORT ON DETERMINATION OF WATER IN FOODS.

By F. C. Weber, *Associate Referee.*

The study of this subject by the association was authorized at the 1905 meeting, when a resolution was adopted instructing the referee on food adulteration to provide for the determination of moisture, studying particularly Benedict's vacuum method.[a] On August 6, 1906, the following circular letter was sent to eleven chemists who had previously signified their interest in this subject, asking their cooperation for the present year:

Dear Sir: At the last meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November 16–18, 1905, the referee on food adulteration was

[a] Benedict and Manning, Amer. J. Physiol., 1905, *13:* 309.

instructed to provide for the determination of moisture, studying Benedict's vacuum method and Maquenne's method.

Please inform me at your earliest convenience if you can assist in this work, so that samples and instructions can be forwarded as soon as possible.

There will be four samples sent out, the moisture to be determined by the methods above and by the method in use in your laboratory.

Respectfully,

F. C. Weber,
Associate Referee on Food Adulteration.

Replies were received from eight chemists, all but two stating that pressure of other duties prevented them from taking up the work at this time, and the two who replied favorably did not send reports. Three collaborators were secured in the Bureau of Chemistry.

The samples selected this year were:

No. 1. Finely bolted rice flour.

No. 2. Durum wheat flour.

No. 3. Potato starch, prepared by grinding in a porcelain mortar.

No. 4. Shredded wheat biscuit, prepared by grinding in a burr mill.

The first three samples were in a fine state of division, while the sample of shredded wheat was somewhat coarser. Each sample was thoroughly mixed and allowed to stand at room temperature for twelve hours before being bottled and sealed with paraffin.

Preparation of the Vacuum.

Benedict in his original method [a] employed the Hemple form of desiccator to obtain a high vacuum by chemical means. One hundred and fifty to 200 cc of concentrated sulphuric acid are placed in the upper compartment of the desiccator and 10 to 20 cc of anhydrous ether, allowed to flow from a pipette, are placed in the bottom of the lower part. After adjusting the top suction is applied, and when the pressure is diminished sufficiently the ether begins to boil, the vapors forcing out the air within the desiccator. When all the air is removed by the suction, the stopcock is closed and the remaining ether vapor is absorbed by the sulphuric acid.

A vacuum of 1 to 4 mm can be obtained by this method in fifteen to twenty minutes. It is essential to have a manometer within the desiccator. It was found advisable to place between the desiccator and the exhaust two wash bottles, the one near the desiccator acting as a trap, while the other contains water through which the ether bubbles, showing the rate at which the system is exhausted. When the water just begins to start back the stopcock on the desiccator is closed.

Recently it was found by H. C. Gore [b] that the Scheibler form of desiccator works equally as well as the Hemple type for the drying of substances in a vacuum. There is no essential difference in the use of these two forms, the sulphuric acid being above the samples in the Hemple desiccator, while in the Scheibler form it is below them. The vacuum is obtained in the same manner, the ether being placed in some convenient receptacle which floats or stands in the sulphuric acid. Inverted ground-glass stoppers, tall enough to be just above the surface of the acid, were found to be quite convenient. Both types of desiccators were used in this work. To avoid errors in weighing samples of this nature in open air, small aluminum dishes, 4.5 cm in diameter and 1.5 cc in depth, provided with a tightly fitting cap of the same material, were employed.

It was hoped that a number of collaborators would respond, that a comparison might be made of the various methods employed in different laboratories for determining water in agricultural products. Simple as this determination may seem, it is one of the chief sources of error in the calculation of analytical results.

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[a] Benedict and Manning, Amer. Chem. J., 1902, *2:* 340.

[b] J. Amer. Chem. Soc., 1906, *28:* 834.

In the third volume of Wiley's Principles and Practice of Agricultural Analysis, 23 pages are devoted to descriptions of methods and apparatus for drying organic bodies. Although the principles involved in each division and subdivision of the methods are practically the same, the application of each method to the same sample would probably give a series of different results, the variations in the details of each method having a marked influence.

Carr and Sanborn[a] in 1895, in an exhaustive study on the desiccation of organic liquids, called the attention of the association to the variation in moisture results. They showed that this variation was caused solely by the decomposition and oxidation of the sample and that it was a function of the temperature to which the sample was exposed. By employing a vacuum oven[b] through which a current of dry air passed, they were able to obtain constant results on sugar solutions (levulose) which remained constant after four hours drying.

Determinations were made in this work under the following conditions:

1. In a partial vacuum (25″–28″) at a temperature of 100° C., through which a slow current of air, dried by passing through sulphuric acid, flowed.
2. In a current of dry hydrogen.
3. In the Hemple and Scheibler vacuum desiccators.

Approximately 1 gram samples were used. The nature of this set of samples is such that the first method very likely gives the maximum results in the shortest time of drying. On inspection of the tables this is seen to be the case, and the results of this method are therefore used as a basis for a comparison of the results obtained by the other methods.

Weighings were made according to the vacuum method at the end of 24 hours, 48 hours, 3 days, 5 days, 7 days, 12 days, and 20 days. In the determinations made in hydrogen, weighings were made at the end of each hour, the maximum time of heating being from 6 to 8 hours.

TABLE 1.—*Moisture determinations in duplicate obtained by drying in air for varying periods.*

Samples.	J. S. Chamberlain.			H. C. Gore.		S. Leavitt.		F. C. Weber.		
	6 hours.	11 hours.	15 hours.	1 hour.	2 hours.	4 hours.	10 hours.	5 hours.	10 hours.	15 hours.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
1. Rice flour	11.60	11.62	11.62	11.67	11.70	11.26	11.46	11.18	11.40	11.42
	11.63	11.67	11.67	11.60	11.62	11.22	11.44	11.24	11.38	11.46
	11.62	**11.64**	**11.64**	**11.64**	**11.66**	**11.24**	**11.45**	**11.21**	**11.39**	**11.44**
2. Durum wheat flour	11.33	11.31	11.32	11.18	11.27	11.06	11.20	11.04	11.20	11.23
	11.35	11.39	11.38	11.16	11.27	10.98	11.18	11.03	11.22	11.24
	11.34	**11.35**	**11.35**	**11.17**	**11.27**	**11.02**	**11.19**	**11.04**	**11.21**	**11.24**
3. Potato starch	14.59	14.56	14.58	14.64	14.60	14.24	14.38	14.33	14.50	14.49
	14.61	14.63	14.63	14.65	14.69	14.14	14.34	14.27	14.46	14.43
	14.60	**14.60**	**14.61**	**14.65**	**14.65**	**14.19**	**14.36**	**14.30**	**14.48**	**14.46**
4. Shredded wheat	9.24	9.28	9.31	8.78	9.08	9.04	9.24	8.99	9.17	9.17
	9.21	9.24	9.25	8.86	9.10	8.94	9.20	9.05	9.20	9.20
	9.23	**9.26**	**9.28**	**8.82**	**9.09**	**8.99**	**9.22**	**9.02**	**9.19**	**9.19**

In Table 1 are given the results of the determinations made in the vacuum oven, through which a current of dry air passed. The temperature of the oven was kept at

[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 47, p. 134, "The dehydration of viscous organic liquids."

[b] Designed by Carr; described in Wiley's Principles and Practice of Agricultural Analysis, *3:* 23.

100° C. and the vaccum at about 25 inches, which corresponds to a water-boiling point of 57°. Thus the water in the samples was exposed to a temperature 43° above the boiling point.

Considerable variation is seen in the time of drying employed by different analysts even in this laboratory. Since the kind of material has the greatest influence on the time of drying, this point should be regulated by future work and not be left to the discretion of the analyst. This is seen in sample No. 1, which contains a high percentage of starch, and No. 3, which is pure potato starch, in which cases drying for 2 hours gave practically the same results as drying for 15 hours, while in samples Nos. 2 and 4 there is a smaller percentage of water obtained by drying for a shorter period of time. The relative fineness of the samples also exerts its influence on this point.

The determinations in the last two instances in this table were made at a later date than the first two and after the samples had accidentally stood a short time, in the laboratory, unsealed.

TABLE 2.—*Moisture determinations obtained by drying in a vacuum for varying periods.*

HEMPLE DESICCATOR.

Analyst.	Sample No. 1.							Sample No. 2.						
	Dried 24 hours.	Dried 48 hours.	Dried 3 days.	Dried 5 days.	Dried 7 days.	Dried 12 days.	Dried 20 days.	Dried 24 hours.	Dried 48 hours.	Dried 3 days.	Dried 5 days.	Dried 7 days.	Dried 12 days.	Dried 20 days.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
J. S. Chamberlain	10.97	11.10	*a* (9.88)	10.83	11.19			10.40	10.42	(9.62)	10.32	10.86		
	11.06	11.21	(10.04)	10.98	11.24			10.40	10.39	(9.45)	10.35	10.82		
Average	**11.02**	**11.16**	*a* **(9.96)**	**10.91**	**11.22**			**10.40**	**10.41**	*a* **(9.54)**	**10.34**	**10.84**		
H. C. Gore		10.95		11.59	11.58				10.67		11.10	10.90		
		11.16		11.61	11.53				10.69		11.12	10.83		
Average		**11.06**		**11.60**	**11.56**				**10.68**		**11.11**	**10.86**		
F. C. Weber	10.19	10.82	10.89											
	10.16	10.63	11.02	10.75	10.96			10.05	10.41	10.12	10.21	9.66		
	10.89	11.25	10.96											
	11.11	11.12	10.90	11.06	11.18			10.27	10.53	10.03	10.16	9.90		
Average	**10.57**	**10.96**	**10.94**	**10.91**	**11.07**			**10.16**	**10.47**	**10.08**	**10.19**	**9.78**		
Maximum					**11.56**							**10.86**		
Minimum					**11.07**							**9.78**		
Average					**11.28**							**10.19**		

Analyst.	Sample No. 3.							Sample No. 4.						
	Dried 24 hours.	Dried 48 hours.	Dried 3 days.	Dried 5 days.	Dried 7 days.	Dried 12 days.	Dried 20 days	Dried 24 hours.	Dried 48 hours.	Dried 3 days.	Dried 5 days.	Dried 7 days.	Dried 12 days.	Dried 20 days.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
J. S. Chamberlain	14.16	14.16	(13.14)	14.02	14.36			6.54	6.98	(6.72)	7.42	8.19		
	14.06	14.06	(13.10)	13.92	14.29			6.48	6.96	(6.76)	7.50	8.12		
Average	**14.11**	**14.11**	*a* **(13.12)**	**13.97**	**14.33**			**6.51**	**6.97**	*a* **(6.74)**	**7.46**	**8.16**		
H. C. Gore		14.33		14.75	14.69				7.86		8.59	8.51		
		14.45		14.76	14.77				7.30		8.10	8.09		
Average		**14.39**		**14.76**	**14.73**				**7.58**		**8.35**	**8.30**		

F. C. Weber	14.34	14.56	14.39	14.27	14.37			6.77	6.76	7.37	7.28	7.23			
								6.68	6.57	7.09					
	14.31	14.56	14.48	14.51	14.51			6.62	7.20		7.33	7.22			
								6.67	7.07	7.00					
Average	**14.33**	**14.56**	**14.44**	**14.39**	**14.44**			**6.69**	**6.90**	**7.15**	**7.31**	**7.23**			
Maximum					**14.73**							**8.30**			
Minimum					**14.33**							**7.23**			
Average					**14.50**							**7.90**			

SCHEIBLER DESICCATOR.

Analyst.	Sample No. 1.							Sample No. 2.						
	Dried 24 hours.	Dried 48 hours.	Dried 3 days.	Dried 5 days.	Dried 7 days.	Dried 12 days.	Dried 20 days.	Dried 24 hours.	Dried 48 hours.	Dried 3 days.	Dried 5 days.	Dried 7 days.	Dried 12 days.	Dried 20 days.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
F. C. Weber	10.94	10.98	11.09	11.09	11.20	(11.73)	11.50	10.58	10.77	10.70	10.48	10.90	(11.21)	11.03
			11.34		11.47					10.76		10.76		
	11.06	11.26	(11.53)	11.34	(11.81)	(11.69)	11.45	10.63	10.74	(10.91)	10.76	(11.37)	(10.55)	11.13
			(11.42)		(11.77)					(10.31)		(10.63)		
Average	**11.00**	**11.14**	**11.22**	**11.22**	**11.34**	**(11.71)**	**11.48**	**10.61**	**10.76**	**10.73**	**10.62**	**10.83**	**(10.88)**	**11.08**
			(11.48)		**(11.79)**					**(10.61)**		**(11.00)**		

Analyst.	Sample No. 3.							Sample No. 4.						
	Dried 24 hours.	Dried 48 hours.	Dried 3 days.	Dried 5 days.	Dried 7 days.	Dried 12 days.	Dried 20 days.	Dried 24 hours.	Dried 48 hours.	Dried 3 days.	Dried 5 days.	Dried 7 days.	Dried 12 days.	Dried 20 days.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
F. C. Weber	14.62	14.46	14.51	14.63	14.73	(14.78)	Lost.	7.25	7.60	7.83	7.83	8.11	(8.49)	8.38
			14.60		14.67					7.79		8.07		
	14.37	14.57	(14.61)	14.59	(14.89)	(14.82)	14.90	7.26	7.49	(7.85)	7.86	(8.50)	(8.19)	8.40
			(14.59)		(14.89)					(7.57)		(8.47)		
Average	**14.37**	**14.52**	**14.56**	**14.61**	**14.70**	**(14.80)**	**14.90**	**7.26**	**7.55**	**7.81**	**7.85**	**8.09**	**(8.34)**	**8.39**
			(14.60)		**(14.89)**					**(7.71)**		**(8.49)**		

[a] Figures in parentheses are results obtained by continuous drying for period of time indicated and represent same samples throughout; 20-day desiccation on separate sample.

In Table 2 the results obtained by drying in the Hemple and Scheibler desiccators are given. The results obtained after standing 7 days in the Hemple desiccator compare very favorably with one another, though in a few instances maximum results are obtained even with 5 days' drying. The maximum results obtained for 7 days' drying are 11.56 per cent for sample No. 1; 10.86 per cent for No. 2; 14.73 per cent for No. 3; and 8.30 per cent for No. 4. The average results are, for No. 1, 11.28 per cent; No. 2, 10.49 per cent; No. 3, 14.50 per cent; and No. 4, 7.90 per cent.

In that part of the table showing the results obtained in the Scheibler type of desiccator the maximum figures show uniformly higher results, being nearly 0.2 per cent higher than the maximum figures obtained in the Hemple form. Further, as the determinations were carried on in this case for periods of 12 and 20 days, the results indicate that drying for 7 days extracts the greatest amount of moisture from the samples. In sample No. 1 there is a gain in weight of the sample after 7 days' drying, No. 2 and No. 3 remain practically constant, while sample No. 4 shows a gain.

TABLE 3.—*Moisture determinations obtained by drying at a temperature of boiling water in a slow current of dry hydrogen.*

No. of sample.	Dried 1 hour.	Dried 2 hours.	Dried 3 hours.	Dried 4 hours.	Dried 6 hours.	Dried 8 hours.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	9.98	10.99	11.13	11.24	11.53	11.79
2	11.17	11.33	11.43	11.46	11.56	Gained.
3	13.63	14.51	14.48	14.51	Gained.	.....
4	8.73	9.04	9.10	9.11	9.21	Gained.

Table 3 gives the results obtained by drying in a current of dry hydrogen at the temperature of boiling water. Determinations were made in duplicate and triplicate, the average only being given. Weighings were made at the end of each hour's drying and continued until the sample gained in weight. The maximum time of drying was 8 hours in the case of sample No. 1, while 4 hours' drying sufficed for sample No. 3.

TABLE 4.—*Comparison of maximum moisture determinations given by each method.*

No. of sample.	Partial vacuum—current dry air.	Hemple vacuum desiccator.	Scheibler vacuum desiccator.	Current dry hydrogen.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
1	11.66	11.56	11.79	11.79
2	11.35	10.86	[a] 11.08	11.56
3	14.65	14.73	14.89	14.51
4	9.28	8.30	8.49	9.21

[a] 20 days in a vacuum.

In Table 4 the maximum results obtained by each method are arranged for comparison. In the samples containing the largest amount of starch, Nos. 1 and 3, the vacuum method gives the highest results, while in the more complex samples, as No. 2, wheat flour, and No. 4, shredded wheat, drying in partial vacuum in a current of dry air gives the highest results. It is not to be inferred from this that the method giving the highest results necessarily gives the exact percentage of hydroscopic moisture. Whether material other than water volatilized at the temperature of 100° C., to which the samples in partial vacuum were exposed, must be determined by a future study of this subject.

It is evident that in a vacuum of 0–5 mm of mercury, which is maintained in the desiccators, there would always be a tendency to establish an equilibrium, the rapidity with which it would be established depending on the volatility of the substances. Under such conditions, there must be a small quantity of vapors of sulphuric acid at

all times within the desiccator, which may exert a slight influence on the determinations.

The fact that determinations made in the Scheibler vacuum desiccator give maximum results at the end of 7 days' drying and then show a gain in weight in nearly all cases after that period, led to the determination of total sulphur in the original samples and in the samples which had stood 12 and 20 days in the desiccator. The sodium peroxid method was employed, the fusion being conducted in nickel crucibles. Three-gram samples were employed in duplicate for the determinations in the original samples, while the vacuum samples were approximately 1 gram. The duplicate determinations agreed closely throughout and a blank on the maximum quantity of sodium peroxid used to complete fusion did not give any sulphur.

The results are given in Table 5, and with the exception of No. 3 the figures are quite striking, showing that this is a factor to be given some consideration, particularly in reference to time of drying. Sample No. 3, which, it will be remembered, is nearly pure starch, gave the highest percentage of water by this method and evidently did not, during the time stated, absorb any of the sulphuric acid. On the other hand, No. 1, rice flour, also contains a high percentage of starch, but shows quite an increase in sulphur content. Sample No. 2 shows an increase of 0.048 per cent during the 12 days, while No. 4 shows an increase of 0.098 per cent. The table also shows that the maximum gain in sulphur takes place within the first 12 days, the results from standing 20 days being practically the same, and very good duplicates of the first set.

TABLE 5.—*Sulphur in samples before and after drying in vacuum desiccator.*

Description.	No. 1.	No. 2.	No. 3.	No. 4.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Original sample	0.103	0.164	0.019	0.129
In Scheibler desiccator 12 days	.141	.212	.017	.227
In Scheibler desiccator 20 days	.142	.210	.024	.222

From the results of the present year's work it is evident that the vacuum method is worthy of careful consideration. The application of the method to a greater variety of materials will secure valuable data as to its value for the determination of water in foods. Recommendations with this end in view and the study of any modifications which may facilitate drying are accordingly made.

RECOMMENDATIONS.

It is recommended that the study of the vacuum method for the determination of water be continued next year.

That the methods employed for study shall be:

The present vacuum method in either the Hemple or Scheibler type of desiccator.

The vacuum method with any modification which may facilitate drying, as the introduction of phosphorus pentoxid as a drying agent.

Drying in a partial vacuum in a current of dry preheated air and inert gases.

The report was referred to Committee C on recommendation of referees.

31104—No. 105—07——5

REPORT ON CEREAL PRODUCTS.

By A. McGill, *Associate Referee.*

The definitions of cereal products authorized by the Secretary of Agriculture[a] are carefully framed so as to employ no words in regard to whose meaning there can be any doubt. Thus, in the definitions of flour and meal, no mention is made of gluten nor of proteids; nor is any minimum of proteid nitrogen fixed. In our present state of imperfect knowledge this is well, but it is undoubtedly to be desired that such a well-known and widely used term as gluten could be given a meaning of sufficient precision to permit of its being employed in connection with flour. It is the word best known to the miller and the baker as representing the valuable and distinctive proximate component of wheat flour. The separation of gluten, the determining of its total amount and of its qualities, are everyday proceedings in all technical laboratories, and especially in such as make a specialty of cereal work.

In the appended notes the recent literature of this subject has been abstracted, presenting very briefly the novel features in the hope that such a definite conception of gluten may be reached as will permit of formulating an acceptable definition.

Gluten.

CONDITIONS AFFECTING GLUTEN ESTIMATION.

The term gluten is applied to the residue obtained by kneading a dough from wheat flour in a stream of water in such a way as to wash away most of the starch, or until the wash water remains practically clear. The operation is incapable of yielding exact results, and when carried out as described can be regarded as affording merely approximate information about the samples of flour tested. Arpin[b] has shown that the percentage of gluten obtained varies with the temperature of the wash water, being higher with warm than with cold water. Thus, on a sample of wheat flour, washed with water at 5° C., he found 7.83 per cent gluten; at 15° C., he found 8.08 per cent, and with water at 25° C. he found 9.24 per cent.

Again, if washing be continued after the removal of the starch, a very considerable loss of gluten occurs. For only five minutes' extra washing[c] he found a loss of 2½ per cent moist gluten (0.9 per cent dry).

Balland has shown that the amount of gluten obtained depends to some extent upon the length of time that the cake of dough is allowed to lie before being washed; and Arpin,[d] while corroborating Balland's observation, shows that the "hardness" of the water used in washing has a great influence on the amount of gluten obtained. He found as much as 4.7 per cent increase (dry gluten) when hard water was employed.

Recognizing the various factors which affect the yield of gluten, Fleurent[e] advises the use of water containing 0.1 gram of calcium carbonate per liter (of course dissolved as bicarbonate) at a temperature of 16° C., kneading the dough for 11 minutes and washing for 2 minutes, finally drying at 100°–105° C. He has found that distilled water reduces the yield of gluten; also that lime as sulphate or chlorid gives a lower yield of gluten than when present as carbonate. Sodium chlorid has a like result. Fleurent also advises that old or acid flour be made neutral with bicarbonate of soda before the determination of gluten.

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[a] Circular 19 of the Secretary's Office, 1906, Standards of Purity for Food Products.

[b] Ann. chim. anal. appl., *7:* 325—Abst. J. Soc. Chem. Ind., 1902, *21:* 1417.

[c] Ann. chim. anal. appl., *7:* 416—Abst. J. Soc. Chem. Ind., 1903, *22:* 168.

[d] Loc. cit. *7:* 376—Abst. J. Soc. Chem. Ind., 1902, *21:* 1560.

[e] Comptes rendus, 1905, 99—Abst. J. Soc. Chem. Ind., 1905, *24:* 155.

COMMENT.

The process of crude gluten estimation quite loses its simplicity, and hence its chief advantage, when all the precautions above described are observed, and it is scarcely to be wondered at that Arpin and others advise the determination of total nitrogen, and the use of a factor for converting this into gluten, as simpler and more reliable than the direct separation of the gluten itself.

CRUDE AND TRUE GLUTEN.

The explanation of the variable results referred to is found in a study of the gluten, as separated by the usual processes. Norton[a] has recently given an excellent résumé of the subject in the Journal of the American Chemical Society. Without attempting to make a full abstract of Norton's paper, it may be said that he distinguishes between crude gluten and true gluten, the latter consisting, according to the researches of Osborne and Voorhees[b] of gliadin and glutenin only. Crude gluten, as usually obtained, contains, in addition to gliadin and glutenin, variable quantities of fiber, starch, and other matters. By using a 1 per cent solution of sodium chlorid Chamberlain[c] obtained a gluten containing 13.19 per cent of nitrogen, equivalent to 75.18 per cent of proteids (N×5.7), or true gluten, in the crude gluten. Analysis of a sample of crude gluten, obtained from a mixture of six durum wheat flours, by the ordinary process of washing, gave Norton[d] the following results:

COMPOSITION OF CRUDE GLUTEN.

	Per cent.
Total protein (N×5.7)	80. 91
Ether extract	4. 20
Fiber	2. 02
Ash	2. 48
Carbohydrates, other than fiber	9. 44
Total	99. 05

Examination of the proteids, by fractional solution, gave the following results:

	Per cent.
Gliadin (70 per cent alcohol extractive)	6 42
Glutenin (0.2 per cent potassium hydroxid extractive)	5. 76
Globulin (10 per cent sodium chlorid extractive)	1. 11
Total proteids recovered	13. 29
Total protein (N×5.7) as recovered directly from the crude gluten	13. 39

The results may be written thus:

Crude gluten.

	Per cent.
Fats, or ether extract	4. 20
Carbohydrates (nonfiber)	9. 44
Fiber	2. 02
Ash	2. 48
Gliadin	39. 09
Glutenin	35. 07

[a] J. Amer. Chem. Soc., 1906, *28:* 8.
[b] Amer. Chem. J., 1893, *15:* 392.
[c] U. S. Dept. Agr., Bureau of Chemistry, Bul. 81, p. 121.
[d] Loc. cit.

	Per cent.
True gluten	74.16
Sodium chlorid, soluble protein	6.75
Total	99.05

The total crude gluten (dry) found was 16.55 per cent of the weight of the flour and the protein found 13.39 per cent.

The content of true gluten corresponds well with that found by Chamberlain, and Norton concludes that crude gluten, as usually prepared, contains approximately 75 per cent of true gluten.

RELATION BETWEEN CRUDE GLUTEN AND TOTAL PROTEIDS.

There is a general agreement between the dry gluten (crude) as found by usual methods and the total protein ($N \times 5.7$) of flours; but closer examination shows that there is a tendency for the gluten to exceed the proteids in straight and low grade flours, to agree closely in patent flours, and to fall short in whole-wheat meal. Norton has carefully examined the causes of this difference, and concludes as follows:

Crude gluten is an expression, in addition to the true gluten content of a flour, of the balance between the loss of nongluten proteids and gain from the retention of nonproteid substances. The relation of the crude gluten content to the total proteid content can thus be explained by the varying composition of the different flours in respect to nitrogenous compounds and nonproteids.

He is of opinion that crude gluten is a very rough expression of the gluten content of a flour or wheat, and the determination has but little worth in the valuation of flours; that, further, the best simple method for ascertaining amount and character of gluten is the determination of total nitrogen, with expression of the ratio of gliadin to total protein.

If we restrict the term gluten to "true gluten" as above defined, the nongluten nitrogen of flour consists of (1) globulin nitrogen, (2) amido nitrogen, and (3) albumen and proteose nitrogen. From the results of work by Norton and Snyder it appears that the following variations occur:

Nongluten nitrogen of total nitrogen.

	Per cent.
Straight durum wheat flour	18.65
Patent spring wheat flour	14.97
Whole durum wheat meal	23.60
Patent spring wheat flours, mean of two samples	13.80
Bakers' grade flour	12.93

VALUATION OF FLOUR.

Kraemer[a] suggests a classification of flours, as follows:

(I) Those that produce a stiff and cohesive dough in the proportion of 14 to 15 grams of flour to 10 cc of water.

(II) Those that do not produce a stiff and cohesive dough under these conditions.

These are further subdivided into:

(A) Those that form a smooth jelly-like paste upon boiling 1 gram of flour with 15 cc of water for about one minute.

(B) Those in which a more or less granular or liquid paste results.

This subclass may be further subdivided into:

(*a*) Those which give off an odor of roasting corn when heated in glycerin to boiling for a few minutes.

[a] J. Amer. Chem. Soc., 1899, *21:* 650.

(*b*) Those not giving such odor.

Guess[a] states that no limit has yet been reached beyond which the increased gliadin content of the gluten is not an improvement in the quality of the flour. In order at once to express the total gluten percentage and the quality of the gluten as regards its gliadin content, Guess suggests a composite factor for denoting the grade or quality of the flour. This composite factor is the per cent of gluten multiplied by the ratio of gliadin to glutenin. In the application of this factor to a large number of flours he found a variation from 58.38 to 15.38, and among whole wheats the following:

No. 1, hard—variation from 27.62 to 10.18.
2, hard—variation from 24.58 to 11.97.
1, Northern—variation from 21.11 to 7.20.
2, Northern—variation from 13.28 to 7.33.

Snyder[b] corroborates the statement of Guess in regard to the importance of the gliadin content, and holds that the gliadin percentage gives a more valuable datum than the gliadin glutenin ratio. He emphasizes the difficulty of estimating gliadin with accuracy, and suggests that gliadin may not itself be a single proteid.

Snyder recognizes the importance of the ash and moisture determinations in fixing the value of a flour for baking, as also the acidity, but acknowledges that no accurate methods exist for determining either moisture or acidity in flours.

The baking test is still the most reliable one in ascertaining the value of a flour in bread making, but the chemical analysis enables nutritive values to be determined.

Color has always been considered as of great value in classifying flours. Snyder[c] points out that, in consequence of artificial bleaching processes, this determination loses much of its value. The blending of bleached low-grade flours with those of higher grades is best detected by determining the ash.

Fleurent[d] points out that ozonized oxygen has no bleaching effect on flour, and peroxid of nitrogen, to the amount of 15 cc to 40 cc per kilo, must be used. The chemical composition of the flour is not changed, so far as known. The action is confined to the yellowish oil of the wheat, but is not a process of oxidation. It corresponds with a lessening of the iodin value, which changed as follows in three samples:

Iodin value.

No. of sample.	Before bleaching.	After bleaching.
1	86.44	81.70
2	86.10	80.79
3	65.20	56.70

The film of oil becomes transparent and permits the whiteness of the starch to show through.

Bleaching by age alone involves oxidation and a precipitation of white, fixed, fatty acids. Fleurent claims that the enzymes of the flour are not affected by bleaching; that the flour keeps better, and that lower grades of flour are not amenable to the treatment.

He outlines a process for the detection of bleached flours, based upon fixation of nitrogen peroxid by the oil. The oil is extracted by petroleum and dissolved in amyl alcohol and treated with alcoholic potash. An orange-red color results with bleached flours. The test is capable of showing as little as 5 per cent of bleached flour in admixture.

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[a] J. Amer. Chem. Soc., 1900, *22:* 263.
[b] Ibid., 1905, *27:* 1068.
[c] Comptes rendus 1906, 180—Abst. J. Soc. Chem. Ind., 1906, *25:* 194.

Wender[a] finds that wheat and other grains contain an enzyme capable of liberating oxygen from hydrogen peroxid and that this enzyme resides chiefly in the embryo and outer coats of the grain. He proposes to use the volume of oxygen liberated in thirty minutes, under fixed conditions, as a measure of the character (fineness) of the flour. He records the following results for 100 grams of substance:

	cc.
Wheat starch	8
Wheat flour	169
Wheat bran	342
Rye flour	153
Rye bran	330
Maize flour	389
Finest wheat flour	128
Coarsest wheat flour	486

Maurizio[b] holds that the aleurometer test is not a trustworthy indication of the value of a flour for baking, although in general the volume of the bread increases as the volume of the gluten. He describes the chemical processes of Robine and Girard as useless, as neither the amount of extractive matter recovered from gluten or flour, nor the specific gravity of solutions in acetic acid and alcoholic potash, indicates the value of a sample to the baker. Nor can fermentation tests replace baking tests. The specific gravity of the bread is of value, and varies as follows:

Best quality	0.23 to 0.28
Medium quality	0.35
Inferior quality	0.46

Liebermann[c] has designed a special apparatus for determining the expansion of gluten on heating in an oil bath to 170° C. for fifteen minutes. Four samples of flour (using 20 grams) gave as follows:

Expansion of flour determined by Liebermann's apparatus.

No. of sample.	Moist gluten.	Expansion.	No. of sample.	Moist gluten.	Expansion.
	Per cent.	*cc.*		*Per cent.*	*cc.*
1	31.6	135	3	24.6	76
2	35.2	120	4	22.3	52

Snyder[d] asserts that flour of good quality should contain 12 per cent of total proteids, or 11 per cent protein ($N \times 5.7$), of which from 55 to 65 per cent should be gliadin.

Norton,[e] commenting on the ordinary methods of ascertaining the bread value of flours, says:

Some workers determine only the dry, crude gluten, others only the moist or wet gluten, whilst others determine both, and express the relation of the two as water capacity. If a gluten has a good water capacity with proper physical qualities it would be desirable, but there does not seem to be anything very definite about the values obtained, and often a high water content goes with excess of glutenin and poor bread-making properties, so that the determination does not seem to be of much value.

The admission that a flour may contain excess of glutenin must be taken as corroborative of the conclusions (already quoted) reached by Guess and Snyder to the effect that excess of gliadin in flour is unknown. Yet in a later sentence Norton seems to

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[a] Zts. Nahr. Genussm., 1905, *10:* 747—Abst. Analyst, 1906, *31*: 73.
[b] Landw. Jahrb., 1902, *31:* 179—Abst. Analyst, 1902, *27*: 249.
[c] Zts. Nahr. Genussm., 1901, *4:* 1009—Abst. Analyst, 1902, *27*: 155.
[d] J. Amer. Chem. Soc., 1904, *26:* 263—Abst. Analyst, 1904, *29*: 157.
[e] J. Amer. Chem. Soc., 1906, *28:* 19.

admit the possibility of an excess of gliadin, when he says: "On the other hand, if the separated gluten lacks body, an excess of gliadin is indicated." Norton advises reporting the gluten as dry gluten, since large personal and other errors enter into the determination of moist gluten.

On the whole, it would seem to be the opinion of Norton, Snyder, Arpin, and other investigators that the crude gluten number has little value in fixing the quality of flour; at least where separation of gluten in the ordinary way is practiced. Fleurent and Manget use a dilute solution of sodium chlorid for washing out the starch, etc. The method is troublesome, and Chamberlain[a] has found it to give too high results.

Macfarlane[b] has recorded results of work on gluten estimation by the following processes:

The dough balls from 10 grams flour stood for 30 minutes and were then washed with 250 cc distilled water; residual gluten, dried and weighed in one case, but duplicate gluten balls, were washed with 250 cc of 70 per cent alcohol, dried and weighed. The resultant weights gave "crude gluten" and "crude glutenin," respectively, and the difference gave "crude gliadin. "Nitrogen was determined in the aqueous washings, and calculated to water soluble proteids; and in the alcoholic washings, and calculated to pure gliadin. The difference between crude gliadin and pure gliadin is designated by Mr. Macfarlane as "dextrinoids." The nitrogen of crude glutenin was determined by the Kjeldahl method, and multiplied by 5.7 to give "pure glutenin." The difference between this number and the crude glutenin number is styled "nonproteids in crude glutenin." The total nitrogen of the flour multiplied by 5.7 gives total proteids.

The proteids found as above described are generally less than the total proteids by about 1.5 per cent; but in certain flours they show an excess of about 0.5 per cent.

If we denominate as "true gluten" the sum of "pure glutenin" and "pure gliadin," as found by Macfarlane, then the "true gluten" found constitutes from about 72 per cent to 94 per cent of the "total proteids" ($N \times 5.7$) of the flour, or from about 70 per cent to about 90 per cent of the crude dry gluten. The number is evidently not comparable with that to which Norton and Chamberlain have given the name "true gluten," and which they found to average 75 per cent of the weight of the crude gluten. Mr. Macfarlane acknowledges that the intelligible appreciation of his analytical results awaits further study.

In a second paper read before the Royal Society this year (May, 1906) Mr. Macfarlane supplements his work by further analytical results on the same lines. Commenting on the difference found between total proteids as calculated from total nitrogen, and from the sum of those obtained in analysis, the author says: "This quantity varies from 0 to 2.52 per cent on the original flour, and may possibly yet afford useful indications as regards the physical character of the gluten from which it is separated." The difference referred to generally shows a loss in washing out the starch, which loss is probably due to glutenin.

Since the wheat crops of 1903, 1904, and 1905 possessed well-recognized characters, as determined by world-wide baking tests, it has been possible for Mr. Macfarlane to interpret his results with reference to the known character of the flours. He finds the most distinctive characteristic to be the gliadin-glutenin ratio, which is 41.07: 58.93 for the best quality of flour (crop of 1903), and concludes: "The most advantageous proportion of gliadin to glutenin for baking purposes is about 40 to 60, it being understood that the proteids removed with the starch in the production of the gluten are to be regarded as glutenin."

This is entirely at variance with hitherto accepted standards; and, as based upon extensive and careful work, practically reopens the whole question.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 81, p. 118.

[b] Trans. Roy. Soc. of Canada, 1905, [2], *11*, Sec. III: 17.

GLIADIN.

As already mentioned, Snyder[a] suggests that gliadin as usually separated may not be a simple proteid.

König and Rintelen[b] have isolated three distinct proteids from the extractive matter obtained by treating gluten with 65 per cent alcohol. According to these investigators, gluten would seem to have the following composition:

Gluten:

A. Insoluble in 65 per cent alcohol=gluten casein (glutenin?).

B. Soluble in 65 per cent alcohol—

I. Gluten fibrin—soluble in 90 per cent alcohol.

II. Mucedin—soluble in 40 per cent alcohol.

III. Gliadin—insoluble in 40 per cent alcohol.

The method by which these separations were effected is much too complex to be available for routine work, and lends probability to a suspicion that changes in the character of the proximate components of gluten may occur during the manipulations.

Snyder[c] describes a method for the direct separation of gliadin from flour by shaking with 70 per cent alcohol, and determination of the gliadin in solution, by means of the polarimeter. He finds that with 15.97 grams of flour and 100 cc of solvent the reading in a 220 mm tube at 20° C. gives a number which multiplied by 0.2 yields a product in close agreement with gliadin nitrogen as obtained by the ordinary Kjeldahl process.

Mathewson[d] has recently made a study of the specific rotation of gliadin. He finds that this is practically independent of the concentration in 70 to 75 per cent alcohol. With 70 to 80 per cent alcohol it decreases with increase in the alcohol strength. Increase in temperature within the limits 20°–45° C. produces a slight increase in the specific rotation. He finds also that the differences in density for gliadin solutions such as would be met with in ordinary analysis are too insignificant to allow a margin for experimental error in this method of determining gliadin. The method was originally suggested by Fleurent.[e]

DETECTION OF FOREIGN STARCHES, ESPECIALLY MAIZE STARCH, IN WHEAT FLOUR.

Kraemer[f] gives special instructions for sampling, mounting, and observing starches, and records the results of treatment with sixteen different reagents in microchemical research. While many starch granules in maize and wheat closely resemble each other, the characteristic forms enable approximate quantitative estimations to be made. He advises the use of polarized light in this kind of work.

He points out that the *odor* of a flour is of value in detecting the presence of maize.

Embrey[g] has found from 10 to 30 per cent of maize in wheat flour, and in "self-raising" flour from 10 to 20 per cent.

He refers to work by White[h] on maize in oatmeal, and to Baumann[i], who points out that 1.8 per cent potash ruptures wheat and rye starch granules without affecting the maize starch, and its action can be immediately stopped by adding acid. This reagent is otherwise superior to chloral hydrate. Embrey makes the microscopic

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[a] J. Amer. Chem. Soc., 1905, *27:* 1068.

[b] Zts. Nahr. Genussm., 1904, *8:* 401.—Abst. Analyst, 1904, *29:* 371.

[c] J. Amer. Chem. Soc., 1904, *26:* 263.—Abst. Analyst, 1904, *29:* 157.

[d] Ibid., 1906, *28:* 624.

[e] Compt. rend., *132:* 1421.—Abst. J. Soc. Chem. Ind., 1901, *20:* 941.

[f] J. Amer. Chem. Soc., 1899, *21:* 650.

[g] Analyst, 1900, *25:* 315.

[h] Ibid., 1895, *20:* 30.

[i] Ibid., 1899, *24:* 150.

test more exact by the use of iodin, or by determining sugar after hydrolysis with sulphuric acid.

In discussion it was brought out that clove oil renders the maize hilum black, while that of wheat remains invisible. Embrey concludes that only roughly quantitative results can be obtained by microscopic work.

Volpino [a] depends upon either an estimation of total gluten, which is much reduced in quantity by admixture of other flours with wheat; or upon estimation of nongluten proteids which are mechanically washed out of the flour. These are recovered from the wash water by asbestos filtration, and nitrogen determined. These proteids (N×6) were found as follows:

	Per cent.
Wheat flour less than	0.2
Maize flour less than	6.5
Barley and rice flours	6.0
Rye flour	5.0

Leroy [b] finds that phoroglucinol colors sawdust much more distinctly than it does the cellulose of flours. Quantitative interpretation of results under the microscope is, however, very unsatisfactory.

Balland [c] has found that the fatty matters of freshly milled flour consist of a very fluid oil and solid fatty acids of different melting points. In the course of time the acidity diminishes and fatty acids increase, the ratio of increase (up to a certain point) being a measure of the age of the flour.

The fatty acids themselves disappear in time and are not found in very old flour. The acidity which is the first indication of alteration of the flour, is not connected with bacterial decomposition of the gluten, but is derived directly from the fat, and occurs in the fat when this is extracted by ether. The gluten is not attacked until the fatty acids produced from the oil begin to disappear. The richer the flour is in oil the more liable to alteration, e. g., flour from hard wheat.

Gudeman [d] points out that the fat in maize flours can not be accurately estimated from a dry gluten mass, as the fat is altered in drying. He prefers rosolic acid as an indicator in determining the acidity of flours.

Watkins [e] shows that a distinct acidity in bread is needed to prevent the development of *Bacillus mesentericus*, which gives rise to the disease called "ropiness." The natural acidity of bread not being sufficient to hinder this development, he suggests the addition of acetic acid in baking, under certain circumstances.

REPORT OF COMMITTEE C ON RECOMMENDATIONS OF REFEREES.

By H. C. Lythgoe, *Chairman*.

(1) Colors.

It is recommended—

1. That, as suggested by the associate referee for 1905, the cooperative work on colors be continued along the following lines:

(*a*) Solubility of the coal-tar and vegetable dyes in various solvents (ether, acetic ether, petroleum ether, methyl and ethyl alcohols, acetone, etc., and mixtures thereof), arranged according to their solubility—as, easily soluble, difficultly soluble, and insoluble.

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[a] Zts. Nahr Genussm., 1903, 1089—Abst. Analyst, 1904, *29:* 89.

[b] Chem. Ztg., 1898, *22:* 311; the Analyst, 1900, *25:* 39.

[c] Compt. rend., 1903, 724.—Abst. J. Soc. Chem. Ind., 1903, *22:* 1303.

[d] U. S. Dept. Agr., Bureau of Chemistry, Bul. 73, p. 42.—Abst. J. Soc. Chem. Ind., 1903, *22:* 764.

[e] J. Soc. Chem. Ind., 1906, *25:* 350.

(*b*) Extractive values of the various solvents for dyes in neutral, acid, and alkaline solutions.

(*c*) Characteristics of the coloring matters as contained in fresh fruits, vegetables, wines, etc., with reagents and solvents, including their respective dyeing properties.

Adopted.

2. It is the sense of the committee that the term "vegetable colors" is a misnomer as applied to the products studied by Mr. Nickles, and the committee recommends that this portion of the report be returned to the referee with the suggestion that the words "commercial colors alleged to be vegetable colors" be substituted for the words "vegetable colors" and that this portion of the report be revised accordingly.

Adopted.

(2) Saccharine Products.

The referee made no formal recommendations, but suggested that if the work on maple products was continued the three methods tried for the determination of the lead number be given a thorough trial [see page 18], and that the work on the malic acid value be continued until a modification is secured which gives more uniform results in the hands of different chemists.

No action was taken by the committee on these suggestions, which are submitted for the information of the referee for 1907.

(3) Distilled Liquors.

It is recommended that a further study be made of the determination of fusel oil.

No action taken by committee, and recommendation goes to the referee for consideration.

(4) Beer.

The following recommendation was not acted upon by the committee, as it involves action as to an official method, and is referred to the referee for 1907 for recommendation as to final action, together with the suggestion made as to the revision of the alcoholometric tables:

I suggest that a committee be appointed by this association for the purpose of revising the alcoholometric tables now given in Bulletin No. 65, that they may be adopted for use at this new temperature (20° C.). I furthermore recommend the adoption of the following methods of beer analysis as official for this association: [See Circular No. 33, Bureau of Chemistry, for detailed statement of methods.]

(5) Infants' and Invalids' Foods.

It is recommended that the subject "Infants' and Invalids' Foods" be dropped.

Mr. Bigelow explained that it was thought best to drop this division of the work for the reason that it was a duplication, nearly all infants' and invalids' foods being included under cereal products, meat extracts, and dairy products.

Mr. Wiley indorsed the view that in general these foods are only general foods which should not be permitted to bear the characteristic name of infants' or invalids' foods, and also called attention to the effort making in the Council of Pharmacy and Chemistry of the American Medical Association to classify medicinal foods; that is, foods never used except in cases of illness or convalescence.

The association accordingly voted to adopt the motion discontinuing the subject as a separate investigation.

(6) Condiments other than Spices.

It is recommended that the methods outlined by the referee [see page 39] be adopted provisionally, but that in printing the same they be given by reference wherever such methods appear under other subjects.

Action deferred for one year.

(7) Tea and Coffee.

It is recommended—

1. That the methods outlined by the referee for the estimation of caffetannic acid [see page 44] be submitted for cooperative study by the members of the association.

Adopted.

2. That the Gomberg method for the determination of caffein be subjected to trial. [See page 45.]

Adopted.

(8) Food Preservatives.

Action on recommendations 1–7 [see page 57] involving changes in the provisional methods in Bulletin No. 65 was deferred until 1907.

The four recommendations as to work for the ensuing year [see page 58] were adopted.

(9) Determination of Water in Foods.

It is recommended that the study of the vacuum method for the determination of water be continued next year and that the methods employed for study shall be: (a) The present vacuum method in either the Hemple or Scheibler type of desiccator; (b) the vacuum method with any modification which may facilitate drying, as the introduction of phosphorus pentoxid as a drying agent; (c) drying in partial vacuum in a current of dry preheated air and inert gases.

Adopted.

(10) General Recommendations.

The committee recommends that the associate referees on the following subjects study the determination of alkalinity of soluble and insoluble ash with a view to obtaining uniform results: Saccharine products, including confectionery; fruit products; wine; beer; vinegar; spices; dairy products (in reference to calcium sucrate in cream); cereal products; vegetables; cocoa and cocoa products; tea and coffee.

Adopted.

At the close of the report of Committee C, Prof. C. E. Munroe, of the George Washington University, welcomed the association to the university halls and in a brief speech invited their cooperation in insuring the success of the proposed exhibit at the Jamestown Exposition, 1907, of the applications of denatured alcohol. Professor Munroe, who has charge of the exhibit, said that its object was educational, and made the following statement in regard to the same:

By act of Congress approved June 7, 1906, alcohol which has been denatured, or rendered unsuitable for drinking purposes, may, from and after January 1, 1907, be used in the arts and industries, and for fuel, light, and power, without the payment of internal-revenue tax, thus making a cheap and inexhaustible source of energy available to our people with which to supplement the coal, petroleum, and gas deposits

which are now being too rapidly drawn upon. To enable our people the more readily to avail themselves of the legislation and to promote invention, through which the largest advantage may be taken of this privilege, an exhibit will be made of the various apparatuses, machines, and appliances by which the heat, light, and power which can be obtained from alcohol may be utilized for domestic, agricultural, and manufacturing purposes, and also of the articles of manufacture into which alcohol enters as a component or factor.

In this connection Doctor Wiley laid before the convention several invitations received from the authorities of the exposition inviting the association to hold the meeting of 1907 at Norfolk under their auspices. Action as to the acceptance of these invitations was deferred.

The report on nitrogen was then presented by the secretary on behalf of the referee.

REPORT ON NITROGEN.

By James H. Gibboney, *Referee.*

The work of the referee for the past year is embodied in the following recommendations of the association adopted at its last annual meeting:

(1) That the study of availability by both the neutral and the alkaline permanganate methods be continued, particularly with the view to determining the amount of material to be used in the neutral method on commercial fertilizers.
(2) That in the official Gunning method for the determination of nitrogen the addition of 0.5 to 0.75 gram of copper sulphate after digesting with sulphuric acid and potassium sulphate for one half hour be studied by the referee. (Fuller.)
(3) That the silver precipitation method (Bul. 46, Rev., p. 14), under "4. Determination of nitrogen," be changed to read as follows: (See Penny's modification, page 77.)

The two samples selected for the nitrogen work were prepared from high-grade acid phosphate, dried blood, and cotton-seed meal: No. 1, acid phosphate and dried blood; No. 2, acid phosphate and cotton-seed meal.

The materials were finely ground and air dried at temperature of laboratory until determinations proved moisture content to be constant. They were then mixed to give approximately a 2 per cent nitrogen content. The average of six determinations of No. 1 (maximum of 2.10, a minimum of 2.08) was 2.09 per cent nitrogen, while that of No. 2 gave (maximum 2.16, minimum 2.12) average of 2.14 per cent nitrogen.

The solution for hydrochloric acid determination, approximately half normal, was prepared by using freshly distilled water and strictly chemically pure acid.

In response to a circular letter asking for cooperation, 36 favorable replies were received from as many laboratories. Sixteen of these sent results which represented the work of 26 chemists.

The following instructions accompanied each set of samples:

INSTRUCTIONS FOR NITROGEN WORK, 1906.

The work on nitrogen for the Association of Official Agricultural Chemists, in which you have expressed your desire to cooperate, includes the following determinations:

Total nitrogen.

(1) Determine total nitrogen by Kjeldahl or Gunning methods.
(2) Determine total nitrogen by Gunning method.
(3) Determine total nitrogen by the following modification of the official Gunning method:

Fuller's modification.—In a digestion flask holding 500 cc place from 0.7 to 3.5 grams of the substance to be analyzed, according to its proportion of nitrogen. Then add 10 grams of powdered potassium sulphate and from 15 to 25 cc of concentrated sulphuric acid. Conduct the digestion as in the Kjeldahl process, starting with a temperature below the boiling point and increasing the heat gradually until frothing ceases. After the digestion has continued for 30 minutes remove the flame and add cautiously 0.75 gram of powdered copper sulphate and continue the digestion to the end. Dilute, neutralize, and distil as in the Kjeldahl method.

Make one determination following above method and one in which 10 cc of strong potassium sulphid solution is added just after diluting, neutralizing, and distilling, as in Kjeldahl method.

Available nitrogen.

(1) *Neutral permanganate method.*—(*a*) Using a charge corresponding to 0.075 gram nitrogen. (*b*) Using a charge of 2 grams sample.

Into a 300 cc low form Griffin beaker weigh 2 grams of the sample if from a mixed fertilizer; if from a concentrated material use a quantity containing approximately 0.075 gram nitrogen. Samples containing materials that have been treated with acid should be washed on a 9 cm S. S. No. 595 filter to 200 cc and transferred, filter and all, to beaker. Digest this with 125 cc of permanganate solution (16 grams of pure potassium permanganate to 1,000 cc water) in a steam or hot-water bath for 30 minutes. Have the beaker let down well into the steam or hot-water and keep closed with a cover glass, stirring twice at intervals of 10 minutes with a glass stirring rod. At the expiration of the time remove from bath, add 100 cc of cold water, and filter through a heavy 15 cm folded filter. Wash with cold water, small quantities at a time, until total filtrate amounts to 400 cc. Dry and determine nitrogen in residue by Kjeldahl method.

(2) *Alkaline permanganate method.*—Weigh out an amount of sample containing 0.045 gram of nitrogen, and transfer to a 600 cc distilling flask. After connecting with condenser to which the receiver containing the standard acid has been attached digest with 100 cc of alkaline permanganate solution (16 grams of pure potassium permanganate and 150 grams of sodium hydrate dissolved in water and made to 1,000 cc) for 30 minutes below the boiling point. Then boil until 85 cc of distillate is obtained. If the material shows a tendency to adhere to the sides of the flask an occasional gentle rotation is necessary during distillation.

Determination of hydrochloric acid—Standard solution, official method.

See Bulletin 46, Rev., p. 14, under "4. Determination of nitrogen." Make duplicate determinations by this method.

Penny's modification.—By means of a preliminary test with silver nitrate solution, to be measured from a burette, with excess of calcium carbonate to neutralize free acid and potassium chromate as indicator, determine exactly the amount of nitrate required to precipitate all the hydrochloric acid. To a measured and also a weighed portion of the standard acid add from a burette one drop more of silver nitrate solution than is required to precipitate the hydrochloric acid. Heat to boiling, cover from the light, and allow to stand until the precipitate is granular. Then wash with hot water through a Gooch crucible, testing the filtrate to prove excess of silver nitrate. Dry the silver chlorid at 140° to 150° C.

Make duplicate determinations by this modification.

Report results under "Total nitrogen" and "Available nitrogen" as per cent nitrogen.

Report results under "Determination of hydrochloric acid" as gram hydrochloric acid per cubic centimeter.

We would be glad to have you comment freely on the working of the different methods, which comments will be incorporated in our report.

James H. Gibboney, *Referee.*
C. L. Penny, *Associate Referee.*

The results of the determinations made by the different analysts appear in the following tables:

TABLE 1.—*Total nitrogen.*

Analyst.	Official Kjeldahl method.		Official Gunning method.		Modified Gunning method ($CuSO_4$).		Modified Gunning method ($CuSO_4$+ K_2S)	
	1	2	1	2	1	2	1	2
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Lewis L. LaShell, Wooster, Ohio	2.06	2.18	2.03	2.11	2.10	2.14	2.16	2.16
	2.09	2.18	2.06	2.13	2.11	2.12	2.16	2.18
S. H. Shieb, Richmond, Va	2.07	2.08	2.14	2.15	2.10	2.12	2.11	2.15
W. D. Cooke, Richmond, Va	2.05	2.09	2.12	2.17	2.14	2.15	.....	.....
F. B. Carpenter, Richmond, Va	2.08	2.10	2.12	2.16	2.12	2.15	.....	.....
W. P. Allen, New Brunswick, N. J	2.08	2.12	2.08	2.14	2.12	2.19	2.12	2.17
	2.07	2.10	2.10	2.14	.....	.....	.....	.....
John Phillips Street, New Brunswick, N. J	2.10	2.18	2.09	2.20	2.07	2.27	.....	.....
	2.12	2.18	2.10	2.24	2.04	2.23	.....	.....
J. O. Mundy, Blacksburg, Va	2.09	2.14	2.07	2.16	2.07	2.17	.....	.....
	.....	2.19	2.10	.....	.....	.....	.....	.....
J. H. Norton, Fayetteville, Ark	.....	.....	2.19	2.21	.....	2.20	.....	2.21
	.....	.....	2.23	.....	.....	2.25	.....	2.19
T. C. Trescot, Washington, D. C	.....	.....	2.13	2.15	2.13	2.13	2.12	2.12
	.....	.....	2.15	2.13	.....	.....	.....	.....
A. W. Blair, Lake City, Fla	2.00	2.05	2.25	2.15	.....	2.18	.....	2.11
	2.05	2.08	.....	2.23	.....	2.05	.....	.....
	2.13	2.18	.....	2.25	.....	.....	.....	.....
James H. Gibboney, Roanoke, Va	2.09	2.14	2.08	2.16	2.10	2.15	2.08	2.16
	2.08	2.16	2.09	2.16	2.11	2.17	2.10	2.15
	2.08	2.14	2.09	2.18	2.13	2.18	2.09	2.17
	2.10	2.15	2.10	2.19	2.10	2.17	2.10	2.17
Geo. A. Olsen and F. W. Woll, Madison, Wis	2.14	2.11	2.11	2.10	2.11	2.15	2.15	2.10
	2.15	2.10	2.12	2.13	2.15	2.07	2.10	2.08
	2.12	2.09	.....	.....	.....	.....	.....	.....
L. Rosenstein, Berkeley, Cal	2.09	2.13	2.09	2.11	2.04	2.11	2.05	2.15
	.....	.....	2.10	2.12	.....	.....	.....	.....
J. E. Greaves, Logan, Utah	1.99	2.16	2.20	2.24	2.18	2.23	2.18	2.18
	1.99	2.18	2.16	2.24	2.16	2.24	2.16	2.18
	.....	.....	.....	.....	.....	2.33	.....	.....
E. B. Holland and P. H. Smith, Amherst, Mass	2.06	2.10	2.15	2.36	2.04	2.13	2.08	2.09
	2.06	2.15	2.08	2.22	2.02	2.08	2.08	2.12
Samuel W. Wiley and W. E. Hoffman, Baltimore, Md	2.08	2.14	2.09	2.13	2.13	2.11	2.10	2.13
	2.10	2.16	2.11	2.15	2.19	2.17	2.13	2.17
	.....	2.17	2.13	2.18	2.22	2.22	2.19	2.21
W. D. Richardson, Chicago, Ill	2.14	2.25	2.35	2.47	2.16	2.30	2.21	2.28
B. F. Robertson, Clemson, S. C	2.13	2.13	2.09	2.13	2.11	2.13	.....	.....
	2.10	2.16	2.12	2.08	.....	2.13	.....	.....
C. C. McDonnell, Clemson, S. C	2.07	2.14	2.10	2.14	2.04	2.15	2.03	2.06
	2.07	2.15	2.10	2.13	2.09	2.13	2.02	2.12
	.....	.....	2.16	2.20	2.18	.....	.....	.....
D. H. Henry, Clemson, S. C	2.08	2.12	2.08	2.20	2.08	2.10	2.10	2.13
	.....	.....	2.02	2.08	1.95	2.09	2.08	2.10
Jerome J. Morgan, College Park, Md	.....	.....	2.09	2.06	2.01	2.09	2.06	2.06
	.....	.....	2.06	2.03	2.02	2.08	.....	.....
	.....	.....	2.06	2.05	.....	.....	.....	.....
C. H. Jones, Burlington, Vt	2.07	2.11	.....	2.14	.....	2.17	.....	2.14
	2.07	2.14	.....	2.17	.....	2.14	.....	2.17
	2.07	2.14	.....	.....	.....	.....	.....	.....
R. W. Thatcher, Pullman, Wash	2.08	2.14	2.08	2.11	2.06	2.08	2.04	2.08
	2.09	2.15	2.06	2.09	.....	.....	.....	.....

TABLE 2.—*Available nitrogen, neutral permanganate method.*

[Two grams of sample=0.075 gram nitrogen.]

Analyst.	Insoluble nitrogen.		Available nitrogen.		Insoluble nitrogen.		Available nitrogen.	
	1.	2.	1.	2.	1.	2.	1.	2.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
W. D. Richardson, Chicago, Ill	1.25	0.36	41.59	84.00	1.32	0.45	38.31	80.00
L. Rosenstein, Berkeley, Cal	.44	.51	.....	.....	.....	.....	.....	.....
	.41	.55	81.06	74.54	.....	.....	.....	.....
E. W. Holland, Amherst, Mass	.88	.20	58.24	90.61	.....	.26	.....	87.75
Samuel W. Wiley and W. E. Hoffman, Baltimore, Md	.27	.16	.....	.....	.....	.....	.....	.....
	.29	.17	.....	.....	.....	.....	.....	.....
	.37	.20	85.17	95.83	.....	.....	.....	.....

TABLE 2.—*Available nitrogen, neutral permanganate method*—Continued.

Analyst.	Insoluble nitrogen.		Available nitrogen.		Insoluble nitrogen.		Available nitrogen.	
	1.	2.	1.	2.	1.	2.	1.	2.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Jerome J. Morgan, College Park, Md.						.29a		
	.18	.16			.24	.43b		82.04
	.21	.14			.26	.39c		
	.19	.16				.18d	87.74	91.75
	.18	.18	91.18	92.23		.16e		
W. P. Allen, New Brunswick, N. J.	.34	.19			.459	.259		
	.32	.17	84.30	91.24	.417	.239	78.94	88.09
John P. Street, New Brunswick, N. J.	.285	.18			.943	.314		
	.41	.17	83.53	91.97	.870	.308	57.01	85.74
S. H. Shieb, Richmond, Va.					.43	.12		
					.43	.13	79.91	93.95
Lewis L. La Shell, Wooster, Ohio.	.93	.17						
	.95	.17	54.59	92.20				
T. C. Trescot, Washington, D. C.	.63	.20	70.56	90.65				
J. E. Greaves, Logan, Utah.	.32	.29						
	.31	.24	84.43	88.01				
A. W. Blair, Lake City, Fla.	.86							
	.64		63.59					
James H. Gibboney, Roanoke, Va.	.31	.15			.39	.23		
	.34	.17			.41	.24		
	.36	.18	83.73	92.57	.44	.27	80.39	88.38
R. W. Thatcher, Pullman, Wash.	.34	.23			.46			
	.26	.23	85.58	89.25	.46		77.84	

TABLE 3.—*Available nitrogen, alkaline permanganate method.*

[Amount taken=0.045 gram N.]

Analyst.	Volatile nitrogen.		Available nitrogen.	
	1.	2.	1.	2.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
W. D. Richardson, Chicago, Ill.	0.87	1.17	40.65	52.00
L. Rosenstein, Berkeley, Cal.	1.17	.87		
	1.12	.80	57.28	39.63
E. W. Holland, Amherst, Mass.	1.27	.95	60.18	44.60
P. H. Smith, Amherst, Mass.	1.24	.92	58.76	43.19
James H. Gibboney, Roanoke, Va.	1.28	1.02		
	1.31	1.04	62.20	47.91
R. W. Thatcher, Pullman, Wash.	.84	.84		
	.88	.84	41.35	39.25
Samuel W. Wiley and W. E. Hoffman, Baltimore, Md.	1.02	.69		
	1.06	.72		
	1.10	.75	50.72	33.33
Jerome J. Morgan, College Park, Md.	1.32	1.05		
	1.29	1.00		
	1.31	1.03	64.22	50.00
C. H. Jones, Burlington, Vt.	1.29	1.03		
	1.29	1.03		
	1.31	1.00	62.64	47.69
S. H. Shieb, Richmond, Va.	1.27	.98		
	1.25	.96		
	1.26	.99	58.88	45.35
Lewis L. La Shell, Wooster, Ohio.	1.11	1.36		
	1.14	1.48	54.59	65.14
T. C. Trescot, Washington, D. C.	1.25	1.12	58.41	52.34
J. E. Greaves, Logan, Utah.	1.23	.92		
	1.14			
	1.16			
	1.16		58.79	42.38
J. H. Norton, Fayetteville, Ark.	1.45	1.41	66.51	63.80
	1.48			
A. W. Blair, Lake City, Fla.	1.32	1.04		
	1.31	1.15		
		.99		
		1.13	63.59	51.43

TABLE 4.—*Determination of hydrochloric acid.*

[Gram per cubic centimeter.]

Analyst.	Official method.	Modified method.
John Phillips Street, New Brunswick, N. J	0.0153659	
	.015-396	
	.0153710	
	.015-142	
	.0153 38	
J. H. Norton, Fayetteville, Ark	.01528	0.01530
	.01526	
T. C. Trescot, Washington, D. C	[a].015229	[b].0151225
G. A. Olsen and F. W. Woll, Madison, Wis	.0153	.0153
	.0153	.0154
Samuel W. Wiley and W. E. Hoffman, Baltimore, Md	.0152535	.0152405
W. D. Richardson, Chicago, Ill	.01524	.01507
James H. Gibboney, Roanoke, Va	.01535	.01533
	.01537	.01537
	.01541	.01539
	.01537	.01536
Jerome J. Morgan, College Park, Md	.01533	.01532
	.01533	.01532
L. Rosenstein, Berkeley, Cal	.01518	.01522
	.01520	

[a] Average of 3 determinations. [b] Average of 2 determinations.

COMMENTS BY ANALYSTS.

J. H. Norton: In the alkaline permanganate method digestion continued only 15 minutes as the solution unexpectedly boiled and it was feared that the standard acid would strike back if the temperature were lowered.

J. E. Greaves: In the alkaline permanganate method on sample 2 the results ran 0.92 to 1.226 per cent, and agreement between the duplicates could only be obtained by distilling off exactly 85 cc. Even after this ammonia is given off until the substance is quite dry.

Jerome J. Morgan: In digesting the sample (2) in determinations *a*, *b*, and *c* with 125 cc neutral permanganate solution as directed it was found that the solution was decolorized. This led to the trial of using 200 cc of the permanganate solution, which gave the results in determinations *d* and *e*. These results check closely with the results on the same sample, using a 2-gram charge.

John Phillips Street: Mr. W. P. Allen and myself both found that bumping caused much trouble when the modified Gunning method was used. Our availabe results were quite satisfactory except on sample 1 when 0.075 gram nitrogen was used, the two sets of results not agreeing with each other at all. We followed your directions in all particulars and in the availability tests washed with 200 cc cold water before adding the permanganate. In standardizing the hydrochloric acid sent, the acid was measured in five 10-cc portions from a 50-cc burette. This burette was marked as having been calibrated, but the results secured caused some doubt as to the accuracy of the calibration. You will notice that the results vary from 0.6043 to 0.6072 gram silver chlorid, too wide a variation to be satisfactory.

S. H. Shieb: The copper sulphate addition in the modified Gunning method is objectionable in that it deposits copper on the zinc during distillation, interfering with the evolution of hydrogen, and thereby causing bumping. The addition of potassium sulphid does not appear to prevent this.

L. Rosenstein: In the hydrochloric acid standardization a 5 per cent solution of silver nitrate was used in precipitating the chlorin.

C. C. McDonnell: A conclusive opinion can not be reached from work on two samples, but from this limited number of determinations the methods in which copper sulphate, and copper sulphate and potassium sulphid were used show no advantage over the official method. In fact the results are more variable and the method slightly more troublesome.

Geo. A. Olsen and *F. W. Woll:* Temperature of hydrochloric-acid solution when drawn from burette, 20° C. All silver chlorid precipitates were dried at 130° C., the highest temperature that could be reached in the bath used.

T. C. Trescot: As you will observe, the results by the modified method (determination of hydrochloric acid) are decidedly lower than those by the official method. In washing with hot water in the modified method I was unable to reach a point where the silver chlorid ceased to dissolve in the wash water.

E. B. Holland and *P. H. Smith:* The addition of copper sulphate in the modified Gunning method, after one-half hour digestion, proved rather a troublesome feature for commercial testing, and in distilling frothed badly, especially where no potassium sulphid was added. Digested two hours.

Neutral permanganate method: This process requires too much time and attention for one in which the results are merely indicative at best. The retarding action of the filter paper during digestion and washing, together with variations in digestion emperature (with our facilities), tends to prevent concordant results.

Alkaline permanganate method: This method is short and simple, but absolutely uniform conditions of digestion and distillation are necessary to obtain agreeing results. Contrary to directions, the time of digestion at this station is taken from the beginning of the ebullition. Distillation almost to dryness (15 cc) is objectionable and often introduces an error. If the quantity of solution were increased to 150 cc (or 200 cc) and 100 cc (or 150 cc) distilled, digestion taken from time of ebullition and perhaps increased to one hour, it would tend toward higher and probably more uniform results.

Comments by Referee.

The modification of the Gunning method suggested by Mr. Fuller was found to be of no advantage, the yield of nitrogen being within a few tenths per cent of the official Gunning method. The difficulties presented by the addition of copper sulphate were two—loss of time in cooling solution down to add the salt and bumping of solution during distillation. This last point was very objectionable and was not decreased to any great extent by the addition of potassium sulphid to remove the copper from solution.

The neutral permanganate method was found to be very tedious and difficult to control. It is full of seemingly insignificant details which when varied cause great variations in the results. For instance, changes in results were obtained by varying the length of time of stirring at the two intervals, by variation in temperature of water bath during digestion (a condition which very often happens unnoticed), length of time required for filtering the digested residue from the permanganate solution, method of washing, and time consumed in washing. The results obtained were too high as compared with availability by actual experiments. From experience with this method relative to quantity of material to be used in commercial fertilizer work I am of the opinion that the proportion of nonnitrogenous organic matter to nitrogenous organic matter should be the determining factor. In the case of sample 1, the charge which gave results nearer field experiments was the one corresponding to 0.075 gram, while in that of sample 2 the charge of 2 grams was found to be nearer the field availability. It would be a very difficult matter indeed to have a sliding variation of quantity of material to be taken for the many materials used as sources of nitrogen. Lack of time prevented a more definite study of this point.

The alkaline permanganate method was found to be much easier to manipulate and control, the only points requiring strict attention being to keep the digestion just below the boil for the thirty-minute period and distilling off the exact 85 cc of solution. The first point was easily controlled after several preliminary tests. The second point always gave more or less trouble, it being very difficult to distil to such a low point. It was found an easy matter to get good duplicates when distillation was

stopped at 85 cc, but, as has often been pointed out, continued distillation after the 85 cc portion will give appreciable quantities of ammonia. Several determinations were made by adding 25 and 50 cc of water just after digestion and distilling 100 cc. Very little variation was found by this procedure.

The standardization of hydrochloric acid by both the official and the modified methods was very satisfactory. No variation was found by the two methods, if the modification can really be called a modification of the official method. This preliminary test to determine the amount of silver nitrate solution within a drop or two was found to be of great value, as less washing was required to remove the small excess of precipitant. Continued washing with hot water was found to be very objectionable, in that very appreciable quantities of silver chlorid were dissolved, passing into the washing. Continued heating of solution during precipitation to collect precipitate was also found to cause a slight variation, due to dissolved silver chlorid. It was found to be very desirable to make the precipitation in a small Erlenmeyer flask, and after adding the desired amount of silver nitrate to wrap in towel and shake vigorously for five minutes. The precipitate was in all cases found to be well collected and the supernatant liquid much clearer than in regular procedure. In all cases I was very careful to keep the volume of my solution small and in no case was it necessary to use 200 cc of hot wash water to remove excess of precipitated nitrates.

Summary.

(1) The Fuller modification, the addition of copper sulphate, and the modification with copper sulphate and potassium sulphid give no increase in yield of nitrogen and introduce several very troublesome features.

(2) The neutral permanganate method gave very variable results in the hands of the different analysts, but with a majority the results were within a reasonable limit. It will appear that in case of sample 1, in which the nitrogen source is dried blood (which contained about 15 per cent nitrogen), the amount of material to be used should be the charge corresponding to 0.075 gram nitrogen. When the 2-gram charge was used the amount of nonnitrogenous organic matter was in much smaller quantity, leaving the permanganate solution stronger and hence more active than where the charge was increased to represent 0.075 gram nitrogen. With sample 2 the reverse was found to be true. The cotton-seed meal contained about 6 per cent nitrogen, hence when a charge corresponding to 0.075 gram was used a greater part of the strength of the permanganate was used up by the nonnitrogenous organic material, materially reducing the activity of the solution and thereby decreasing the availability percentage.

The results by the alkaline permanganate method compare very closely and, while somewhat low, the method presents greater possibilities than the neutral procedure.

The results obtained in the standardization of hydrochloric acid were very satisfactory. In no case was there a variation among different analysts that could not be explained either by the method of drawing sample from burette or variation in calibration and different temperature of liquid when drawn from burette. The modification no doubt served a good purpose in determining almost the exact amount of silver nitrate solution required.

Recommendations.

It is recommended:

(1) That the work on the Fuller modification of the official Gunning method be discontinued and that the Gunning method remain as it is now stated.

(2) That the work on the neutral permanganate method be continued along the same lines as this year, having in mind the influence of excessive amounts of nonnitrogenous material in the source of nitrogen; that work be directed along the line

of eliminating some of the many details of the method which influence to too great a degree the results obtained.

(3) That the work on the alkaline permanganate method be continued and that the quantity of material taken be changed to 0.0675 gram nitrogen; that the quantity of alkaline permanganate used in digestion be changed to 150 cc, and that 100 cc be distilled off before titration.

The modified method should read:

Weigh out an amount of sample containing 0.0675 gram of nitrogen and transfer to a 600 cc distilling flask. After connecting with condenser to which the receiver containing the standard acid has been attached, digest with 150 cc of alkaline permanganate solution (16 grams of pure potassium permanganate and 150 grams of sodium hydrate dissolved in water and made to 1,000 cc) for thirty minutes below the boiling point. Then boil until 100 cc of distillate is obtained. If the material shows a tendency to adhere to the sides of the flask, an occasional gentle rotation is necessary during distillation.

(4) That the Penny modification be added as a footnote to "4. Determination of nitrogen," standard acid solution.

That the method for standardization be changed in the following points:

(*a*) That the amount of solution taken for determination should be 10 cc, drawn from burette at 20° C., for half normal solutions, and proportionate amounts for stronger or weaker solutions.

(*b*) That the amount of water used in washing silver chlorid precipitate be changed from 200 cc to an amount necessary to eliminate excess of reagent.

(*c*) That the precipitation be made in a small Erlenmeyer flask so that after precipitation the contents of flask can be shaken vigorously for five minutes and the solution filtered immediately on settling.

THE DETECTION OF PEAT IN COMMERCIAL FERTILIZERS.

By John Phillips Street.

Recently several manufacturing plants have been established for the drying and pulverizing of peat, and it is claimed that it is the intention to use it as a drier in mixed fertilizers, and as a diluent of dried blood. While this use of peat may serve a valuable end in improving the mechanical condition of fertilizers, it also offers a temptation to the manufacturer to depend upon it, at least in part, for his nitrogen supply. Recent analyses of 123 samples of New Jersey peat show a range of from 0.74 to 2.83 per cent of nitrogen, with an average of 1.75 per cent. The inertness of peat nitrogen is well established, and the possibility of its utilization in the compounding of commercial fertilizers is, therefore, a matter of considerable importance.

Von Feilitzen and Tollens[a] have shown that pentosans are quite generally present in peat. Fifteen samples analysed by them contained from 2.65 to 12.75 per cent of pentosans, those taken from the upper and less decomposed layers containing the highest percentages. These high percentages were as a rule accompanied by relatively high percentages of nitrogen. These facts suggested to the writer the possibility of employing the phloroglucin method, as used for the determination of pentosans in cattle feeds, as a means of detecting the presence of peat in commercial fertilizers.

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[a] Ber. d. chem. Ges., 1897, *30:* 2571.

Seven samples of peat, differing widely in nature and mechanical condition, were analysed with the following results:

Analyses of seven samples of peat.

Sample No.	Total nitrogen.	Pentosans.	Sample No.	Total nitrogen.	Pentosans.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
1	0.91	2.32	5	2.65	4.98
2	1.21	1.57	6	2.72	2.57
3	2.05	2.91	7	2.98	3.56
4	2.14	8.74			

The pentosans ranged from 1.57 to 8.74 per cent, with an average of 3.81 per cent, a high percentage of nitrogen and pentosans in general being associated together.

The only material commonly used as a source of organic nitrogen in fertilizers, which might supply a considerable quantity of pentosans, is cottonseed meal, and this material has a very limited use in fertilizers in the northern and eastern markets. Average samples of tankage and dried blood were tested for pentosans, and were found to contain 0.75 and 0.47 per cent, respectively; this was in all likelihood partially due to an accidental contamination in both cases. Besides, the official method for pentosans is hardly applicable where such small quantities of furfural are obtained; 3 grams of the tankage yielded only 0.0204 gram of phloroglucid and the same amount of blood yielded 0.0106 gram. The pentosan determination apparently gave high results with these two fertilizers, and it is doubtful if either contains more than a trace.

Three mixtures were prepared as follows:

Mixture No. 1. One part each of nitrate of soda, dried blood, and tankage; 5 parts of acid phosphate, and 2 parts of muriate of potash. It contained 3.27 per cent of nitrogen (1.57 as nitrates); 9.42 per cent of phosphoric acid, 10.09 per cent of potash, and 0.12 per cent of pentosans.

Mixture No. 2. One part each of nitrate of soda, dried blood, tankage, and peat (No. 5); 4 parts of acid phosphate, and 2 parts of muriate of potash. It contained 3.53 per cent of nitrogen (1.57 as nitrates), 7.98 per cent of phosphoric acid, 10.09 per cent of potash, and 0.62 per cent of pentosans.

Mixture No. 3. One part each of nitrate of soda, dried blood, and tankage; 3 parts of peat; 2 parts of acid phosphate, and 2 parts of muriate of potash. It contained 4.06 per cent of nitrogen (1.57 as nitrates), 5.10 per cent of phosphoric acid; 10.09 per cent of potash, and 1.62 per cent of pentosans.

These mixtures represented in composition high-grade fertilizers, the first containing no peat, the second 10 per cent of peat, and the third 30 per cent. It is doubtful if as small a quantity of peat as 10 per cent would be used in actual practice, but it was used here to test the delicacy of the method.

Pentosans were determined in each of the mixtures by the phloroglucin method. No. 1 yielded a trace; No. 2, 0.52 per cent, and No. 3, 1.41 per cent. These figures are slightly below theory, but show very fair agreement when the difficulties of the method are taken into consideration. It is seen, therefore, that a pentosan determination will indicate as small an addition as 10 per cent of peat. If cottonseed meal, or castor pomace were used to compound the fertilizer, the test for pentosans would not establish with any certainty the use of peat, for these materials both contain pentosans. However, these materials are used but little in the northern States (excepting castor pomace in tobacco fertilizers), and it is believed that this simple test will in the great majority of mixed fertilizers indicate whether or not peat has been used; it will likewise serve for the detection of peat in dried blood.

After the close of the meeting the following paper was received by the secretary, in the transmission of which Mr. Gladding said:

The question arises whether a composite method such as I suggest, a combination of the present official Kjeldahl and Gunning methods, is official per se by virtue of the official character of the two component methods. If not, I wish that such a combination method could be formally declared official, as I wish to use it in my laboratory on account of its far greater reliability. Will you kindly see that the proper action is taken in this matter?

The report is accordingly submitted for the information of the referee on nitrogen without instructions from the association.

COMPARATIVE WORK ON NITROGEN ESTIMATIONS BY THE KJELDAHL AND GUNNING METHODS AND BY A COMBINATION OF THE TWO METHODS.

By Thomas S. Gladding.

A number of fertilizers of all kinds—blood, tankage, fish scrap, humus, etc.—received in the course of business have been recently examined for nitrogen by either the official Kjeldahl or Gunning method and at the same time a comparative analysis has been made by a combination of the two methods as follows:

COMBINATION METHOD.

One gram of fertilizer; 25 cc of sulphuric acid; 10 grams of potassium sulphate; 0.7 gram of mercuric oxid; heat till water white. Cool, add 200 cc of water, 0.5 gram of zinc dust, 25 cc of potassium sulphid solution, 50 cc of soda solution, and distil.

The results of the 81 comparative analyses given in the following table show an almost uniformly higher percentage of nitrogen by the combination method. The average excess is 0.06 to 0.08 per cent. In many individual cases the excess is 0.20 per cent. Our experience shows that the combination method is more rapid and more reliable.

Comparison of nitrogen determinations made by the Kjeldahl, the Gunning, and the combination methods.

Kjeldahl method.	Combination method.	Kjeldahl method.	Combination method.	Gunning method.	Combination method.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
8.56	8.61	4.40	4.42	10.91	11.04
16.11	16.26	15.66	15.71	16.21	16.26
12.06	12.01	11.66	11.66	14.91	15.06
10.57	10.67	2.02	2.02	10.46	10.46
9.61	9.76	6.15	6.18	9.46	9.61
9.06	9.11	6.85	6.90	8.25	8.30
16.51	16.61	9.71	9.81	6.31	6.36
11.66	11.76	4.33	4.40	12.21	12.26
8.35	8.25	7.70	7.80	5.70	5.85
7.16	7.06	8.55	8.50	7.45	7.40
11.71	11.91	10.01	9.91	11.81	12.06
15.41	15.61	2.85	2.85	6.23	6.30
15.66	15.71	9.75	9.85	11.46	11.56
8.26	8.31	9.46	9.56	9.31	9.46
11.66	11.71	11.46	11.41	4.10	4.20
11.81	11.91	11.76	11.86	7.81	7.81
7.85	7.90	7.86	7.81	10.26	10.41
9.01	9.01	11.66	11.86	5.27	5.32
5.41	5.46	11.96	12.11	8.86	8.91
7.06	7.06	6.75	6.90	1.50	1.55
10.41	10.36	4.15	4.25	10.56	10.61
8.66	8.66	8.41	8.41	10.96	11.01
11.96	12.06	9.51	9.61	9.46	9.51
7.66	7.71	14.61	14.76	.....	.....
13.71	13.81	9.91	10.01	.....	.....
6.20	6.25	1.97	2.02	.....	.....
11.36	11.46	9.36	9.56	.....	.....
9.31	9.41	8.86	9.01	.....	.....
.....	.....	8.26	8.36	.....	.....
.....	.....	4.30	4.30	.....	.....
10.456	10.515	8.33	8.39	9.107	9.187

REPORT ON THE SEPARATION OF NITROGENOUS BODIES IN CHEESE.

By R. Harcourt, *Referee.*

Last year collaborative work was done with the method proposed by Van Slyke and Hart for the separation of nitrogenous bodies in cheese.[a] The results obtained and reported [b] showed some variations in the amount of nitrogen secured in the water extract and very wide differences in the quantity obtained from the extraction with the salt solution. Further study showed that in nearly every case complete extraction was not secured and that the cotton wool filter did not make a complete separation of all the insoluble nitrogenous bodies. It is evident that until complete extractions and filtrations of the soluble nitrogenous substances are obtained there is little use of doing collaborative work on the separation of the various nitrogenous bodies contained in the solution. Consequently, it was decided to confine the work of this year, first, to a study of the amount of water required to make a complete extraction, and, second, to improving the method of filtering.

Before preparing the following sheet of instructions several methods of filtering and centrifugal force were experimented with to ascertain the most efficient and rapid method of securing a clear filtrate. The use of an asbestos pad, about one-quarter of an inch thick, on a Wilt plate or a Hirsch funnel, attached to a strong filter pump, gave us the best results, and this method was accordingly selected for the cooperative work.

INSTRUCTION SHEET.

Sampling.—Thoroughly mix the contents of the bottle before taking sample.

Extraction of water-soluble products.—In a porcelain mortar, thoroughly mix 25 grams of cheese sample, prepared as indicated above, with about an equal bulk of clean quartz sand. Transfer this mixture to a 450-cc Erlenmeyer flask, to which add about 100 cc of distilled water at a temperature of 50° C. The flask is placed on a water bath or in some place where it can be kept at a temperature of 50° to 55° C., and is allowed to stand for half an hour, being vigorously shaken from time to time. The liquid portion is then decanted through a filter of absorbent cotton into a 500-cc flask. The residue is again treated with 100 cc of water, heated, agitated, and the liquid decanted as before. This process is repeated until the filtrate, after being cooled to room temperature, amounts to 500 cc, exclusive of the fat, which usually is present at the top of the liquid.

After the 500 cc of water extract has been obtained, filter through a thick pad of asbestos on a Wilt plate or Hirsch funnel. Determine the nitrogen by the Kjeldahl method, in an aliquot portion of the solution, (*a*) before passing through the asbestos pad and (*b*) after passing through the asbestos pad.

Continue the extraction of the insoluble residues with another 500 cc of water in the same manner as before, and, after filtering through the asbestos pad, determine the nitrogen in an aliquot portion.

The cotton filter mentioned is made of two layers of absorbent cotton, prepared as follows: In a glass funnel, place some absorbent cotton to the depth of about 1 inch, moisten with water, in order to compact it, and then above this place another layer of cotton of the same thickness. Upon this pour the portions of cheese extract. This kind of filter allows rapid filtration without the aid of a pump, and is as effective in every way as paper, which requires half a day or more for complete filtration of 500 cc of extract. Several samples of cheese can be extracted at the same time. The upper layer of cotton holds all solid particles and can be returned to the flask for extraction with salt solution.

Extraction of salt-soluble products.—Place the upper layer of cotton in the flask with the residue from the water extraction. Extract with several portions of a 5 per cent solution of sodium chlorid, the process being carried out both with regard to temperature and method of filtering the same as in preparing the water extract. Filter through the asbestos pad and determine the nitrogen by the Kjeldahl method before and after passing through the asbestos pad.

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 73, p. 87, Proceedings of 1902.

[b] U. S. Dept. Agr., Bureau of Chemistry, Bul. 99, p. 125, Proceedings of 1905.

Continue the extraction of the insoluble residue with another 500 cc of the 5 per cent salt solution, filter through an asbestos pad, and determine nitrogen as before.

Report the duplicate work in nitrogen as percentages of weight of cheese taken.

Eleven chemists signified their willingness to cooperate in the work, and, in June, two samples of cheese were sent to each one, together with a copy of the above instructions. For various reasons, only four of those who received samples were able to make complete returns. The results are as follows:

Results of cooperative work on determination of nitrogen in cheese.

Determination.	E. G. de Coriolis, Guelph, Ontario.		A. W. Bosworth, Geneva, N. Y.		A. W. Dox, Storrs, Conn.		B. Pilkington, Corvallis, Oreg.	
	1	2	1	2	1	2	1	2
Water extract:	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
First 500 cc through cotton wool alone	0.946[a]	0.748	1.07	1.06	1.16	0.97	1.101	1.145
	.930	.714	1.08	1.05	1.12	.....	1.067	.927
First 500 cc through cotton wool and asbestos	.857	.661	1.09	1.07	1.11	.96	.946	.922
	.862	.661	1.09	1.04	1.11	.96	.966	.921
Second 500 cc through cotton wool alone	.141	.112	.18	.18	.....	.....	.078	.179
	.141	.140	.18	.20	.....	.....	.078	.185
Second 500 cc through cotton wool and asbestos	.117	.140	.15	.....	.10	.12	.....	.199
	.124	.140	.14	.17	.10	.11	.....	.208
Salt extract:								
First 500 cc through cotton wool alone	1.098	1.350	.59	.....	1.37	1.83	.988	1.438
	1.098	1.355	.59	1.42	1.37	1.84	.949	1.314
First 500 cc through cotton wool and asbestos	1.042	1.305	.54	1.40	1.34	1.80	.724	1.117
	1.047	1.316	.52	1.44	1.35	1.81	.724	1.117
Second 500 cc through cotton wool alone	.386	.476	.32	.34	.....	.....	.674	.517
	.381	.482	.33	.37	.....	.....	.701	.494
Second 500 cc through cotton wool and asbestos	.386	.426	.33	.33	.52	.32	.612	.589
	.386	.426	.33	.33	.52	.32	.623	.613

[a] The cheese was mailed to the various collaborators during very hot weather. The sample used by Mr. de Coriolis was kept at a temperature of 40° F. until the work was commenced. This difference in temperature and the changes it would induce doubtless explain why he recovered a smaller amount of water-soluble nitrogen. However, this does not destroy the value of results, as the only points studied were with reference to the completeness of the extraction and filtration.

The above figures clearly show that the 500 cc of water proposed in the original method were not sufficient to make a complete extraction of the water-soluble nitrogenous substances. With comparatively "green" cheese the 500 cc of water may be sufficient, but when the cheese is well ripened there is a tendency for the material to gather into a glue-like mass which prevents the extraction of the soluble compounds. In the case of the salt solution extraction there is so much nitrogen recovered in the second 500 cc that it is quite possible that even more than 1,000 cc of the solution should have been used in making the extract.

With reference to the method of filtering, it is evident that two of the workers were able to make a complete separation of the soluble bodies by means of the cotton wool. In our own work we have found it convenient to manipulate the cotton filter so as to cause no delay in the extraction, even if some of the finer particles of insoluble matter do pass into the filtrate, and then after the full extraction has been made to draw the whole filtrate through a thick pad of asbestos on a Wilt plate or Hirsch funnel. The fat is retained by the cotton and the filtration through the asbestos can be made quickly and insures a perfectly clear filtrate.

Recommendations.

It is recommended:

(1) That the original method of preparing the water extract, proposed by Van Slyke and Hart, be so altered as to call for the use of 1,000 cc of water in place of 500 cc.

(2) That the method of drawing the water extract through a thick pad of asbestos, after it has been separated from the fat and insoluble nitrogenous matter by cotton wool, be further studied.

(3) That the temperature at which the extraction is made be further studied.

(4) That the completeness of the extraction of matter soluble in salt solution be further studied.

The report of the referee on the separation of vegetable proteids was not received until after the association had adjourned, but is here inserted in its logical sequence.

REPORT ON THE SEPARATION OF VEGETABLE PROTEIDS.

By Harry Snyder, *Associate Referee.*

In the separation of the alcohol-soluble proteids of wheat and flour a 70 per cent solution of alcohol is employed. Some analysts prepare the solution by volume and some by weight. Osborne and Voorhees,[a] in discussing the properties of gliadin, state: "In absolute alcohol the proteid (extracted by dilute alcohol) is entirely insoluble, but dissolves on adding water, the solubility increasing with the addition of water up to a certain point, and then diminishing. The exact degree of solubility has not been determined for various strengths of alcohol, but mixtures of about 70 per cent of alcohol and 30 per cent of water dissolve the proteids in almost indefinite amount."

The absolute strength of the solution which they employed does not appear to be given. The subsequent treatment which the alcohol-soluble proteids received was such as to prevent the presence of other proteids. In their work it was not the specific aim to make a quantitative separation of the proteid, but to secure it in as pure a form as possible for analysis.

Teller found the amounts of nitrogen dissolved by different strengths of alcohol to be as follows:

Amounts of nitrogen dissolved by varying strengths of alcohol.

Alcohol by volume.	Alcohol-soluble nitrogen.	Alcohol by volume.	Alcohol-soluble nitrogen.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
95	0.21	65	1.30
90	.31	60	1.38
85	.61	55	1.40
80	.89	50	1.40
75	1.08	45	1.40
70	1.18	40	1.40

Because of the lack of constancy in the amount of the alcohol-soluble nitrogen Kjeldahl has seriously doubted the existence of a definite proteid known as gliadin, and regarded the alcohol-soluble proteid as "spit off" from the general mass of wheat proteids. Other investigators have expressed a similar view.

An examination of the results available shows that alcohol of 0.90 specific gravity (65 per cent by volume and 58 per cent by weight) extracts from one to two-tenths of a per cent more nitrogen than alcohol that is 10 per cent stronger. The maximum amount appears to be dissolved by alcohol of 40 to 60 per cent strength, but this alcohol also extracts the maximum of other proteids.

The following amounts of nitrogen were obtained by alcohol of 60 to 72 per cent strength by weight in the Minnesota Experiment Station Laboratory:

[a] Amer. Chem. J., 1893, *15*: 438.

Nitrogen dissolved by 60–72 per cent alcohol.

Alcohol.	Nitrogen.
Per cent.	*Per cent.*
60	0.85
68	.74
70	.70
72	.67

Mr. Frank T. Shutt, chemist of the Department of Agriculture of the Dominion of Canada, from whom the sample was obtained, reported 0.70 per cent of nitrogen soluble in 0.70 per cent alcohol by weight.

In a second sample of high grade Minnesota patent flour the following results were obtained by Mr. Hummel, assistant chemist of the Minnesota experiment station:

Nitrogen results obtained under varying conditions of extraction (Hummel).

Alcohol by weight.	Nitrogen dissolved.	Time of extraction.	Alcohol by weight.	Nitrogen dissolved.	Time of extraction.
Per cent.	*Per cent.*	*Hours.*	*Per cent.*	*Per cent.*	*Hours.*
70	0.95	24	75	0.68	24
70	.97	30	75	.65	44
72	.88	24	81	.33	24
72	.90	30	81	.35	44

Mr. Shutt also reported the following results on another sample of flour:

Gliadin nitrogen dissolved by varying strengths of alcohol (Shutt).

Solvent alcohol.	Gliadin nitrogen.	Solvent alcohol.	Gliadin nitrogen.
Per cent by weight.	*Per cent.*	*Per cent by weight.*	*Per cent.*
60	0.94	75	0.60
62.5	.93	76.8	.66
65	.92	86.4	.12
70	.83		

The analyses given in the table below were transmitted by Mr. Shutt with the following comment:

The "baking strength" was obtained by the cereal division of the Central Experiment Farm. All of the other data are from the chemical laboratory.

I have arranged the flours in three orders, according to (1) total protein, (2) gliadin, (3) dry gluten. You will observe that we have in these data a very strong indication if not a proof of the close relationship between these determinations. A year or two ago we made a number of estimates of gliadin nitrogen, extending the time of extraction and varying the agitation and the solvent to which the flour was subjected. We did not, however, find any material increase arising from thus prolonging the extraction or from the extraordinary shaking.

In an earlier letter Mr. Shutt stated that he believed that lack of care in the matter of the strength of the alcohol employed as a solvent was the cause of the lack of uniformity of gliadin results obtained by different workers.

Analysis of flours, April, 1906 (Shutt).

[70 per cent alcohol.]

No.	Designation.	Albuminoids (N × 5.7).	Gliadin (N × 5.7).	Albuminoids in the form of gliadin.	Gluten.		
					Wet.	Dry.	Ratio of dry to wet.
		Per cent.	*Per cent.*	*Per cent.*	*Per ct.*	*Per ct.*	
81	Aurora, C. E. F., 1905	10.60	4.56	43.02	36.79	12.01	3.06
83	Red Fife H., C. E. F., 1905	13.33	6.49	48.68	43.07	14.09	3.06
85	Soft Red Fife, Man., 1905	9.17	3.93	42.85	28.67	10.62	2.70
86	Hard Red Fife, Man., 1905	11.79	5.64	47.82	41.45	14.89	2.79
87	Assiniboia, Man., 1905	9.40	4.21	44.78	32.26	10.97	2.94
88	Huron (selected) C. E. F., 1905	13.22	6.61	50.00	44.14	15.13	2.91
90	8 C., C. E. F., 1905	15.50	8.03	51.80	54.22	17.89	3.03
91	9 J. 3, C. E. F., 1905	14.39	7.18	49.89	58.57	18.70	3.13
92	Turkey Red, fr. Kansas	16.13	7.29	45.18	57.63	18.05	3.19
95	Advance, C. E. F., 1905	14.42	6.72	46.60	49.37	17.36	2.84
98	Laurel, C. E. F., 1905	11.51	6.04	52.47	42.55	16.17	2.63
99	Colorado No. 50 fr. Colorado	13.96	6.38	45.70	45.62	18.67	2.44

No.	Designation.	Physical characteristics.	Baking strength (C. E. S.).
81	Aurora, C. E. F., 1905	Good quality; resilient	91.0
83	Red Fife H., C. E. F., 1905	do	98.5
85	Soft Red Fife, Man., 1905	do	89.0
86	Hard Red Fife, Man., 1905	do	100.0
87	Assiniboia, Man., 1905	Yellowish; lacking somewhat in cohesiveness	91.5
88	Huron (selected) C. E. F., 1905	Lacking somewhat in resiliency	87.5
90	8 C., C. E. F., 1905	Good, but slightly sticky	95.0
91	9 J. 3, C. E. F., 1905	Flabby, soft, very sticky, nonresilient	79.0
92	Turkey Red, fr. Kansas	Good quality; resilient	100.0
95	Advance, C. E. F., 1905	do	91.0
98	Laurel, C. E. F., 1905	do	77.0
99	Colorado No. 50, fr. Colorado	Good, but rather granular and lacking somewhat in elasticity.	94.0

Recommendation.

There is a close agreement between the results obtained upon the same sample of flour by the two laboratories reporting, and there is also a uniformity in the results secured when the strength of the alcohol is varied and different samples of flour used, i. e., there is a decrease in the alcohol-soluble nitrogen with increase in strength of solvent.

To secure greater uniformity of results, it is recommended that for the extraction of alcohol-soluble nitrogen in wheat and flour 70 per cent alcohol by weight, specific gravity 0.871, be employed.

On behalf of the Washington Section of the American Chemical Society, an invitation was extended to the association to be present at the meeting of the section to be held at the Cosmos Club, November 15, the subject under discussion being denatured alcohol, with a paper on the new denatured alcohol law and its effects, by Mr. C. A. Crampton of the Treasury Department.

The association adjourned.

SECOND DAY.

THURSDAY—MORNING SESSION.

At the opening of the morning session Vice-President Street took the chair and President Hopkins delivered the annual address, upon the subject "The duty of chemistry to agriculture." This address has been printed as a circular of the Illinois station and is omitted here.

At the close of the president's address the following committees were announced:

APPOINTMENT OF COMMITTEES.

Committee on resolutions: Messrs. Van Slyke, Tolman, and Allen.

Committee on amendments to the constitution: Messrs. Winton, A. M. McGill, and Veitch.

Committee on nominations: Messrs. Woods, Peter, Woll, Blair, and Frear.

Committee A on recommendations of referees: Messrs. Davidson, Hartwell, McDonnell, Magruder, and Penny.

Committee B on recommendations of referees: Messrs. Holland, Kebler, Bartlett, Robison, and Woll.

Committee C on recommendations of referees: Messrs. Lythgoe, Bigelow, Doolittle, Cochran, and C. D. Howard.

Committee on revision of methods: Messrs. Haywood, Veitch, Tolman, Winton, Street, Woll, and Pettit. (This committee had been appointed before the meeting in order that a report might be presented.)

Committee to invite the Secretary and Assistant Secretary of Agriculture to address the association: Messrs. Davidson, Hardin, and Patterson.

REPORT ON THE SEPARATION OF MEAT PROTEIDS.

By F. C. Cook, *Associate Referee.*

To those who signified a willingness to cooperate, a sample of a commercial meat extract, together with directions for the work, was sent on July 25, 1906. Cooperators were asked to keep the sample cold and to commence the work as soon as possible, conducting it according to the following directions:

DIRECTIONS FOR MEAT EXTRACT ANALYSIS.

Insoluble and coagulable proteid.—Use 8 grams of the sample in duplicate, dissolved in 75 cc of distilled water. Make neutral to litmus (test neutrality, taking a drop outside, by means of a capillary tube, on a piece of delicate litmus paper) by adding

dilute alkali, tenth-normal preferred. Report number of cubic centimeters of tenth-normal alkali per 100 grams of sample. Acidify the neutral solution by adding 10 cc of tenth-normal acetic acid and make the total volume up to 120 cc. Coagulate by boiling for two minutes. After cooling, filter and wash with distilled water. Determine the nitrogen in the precipitate, which is that of the insoluble and coagulated nitrogen. The filtrate is made up to 150 cc volume and divided into three 50 cc aliquots.

Albumoses at room temperature.—Transfer one 50 cc aliquot to a Kjeldahl flask, add three drops of sulphuric acid, and saturate with zinc sulphate, shaking frequently. Have 1 gram of zinc sulphate undissolved in the bottom of the flask. Let stand over night, filter and wash with saturated zinc sulphate solution after having rinsed the flask out with a portion of the saturated zinc-sulphate solution. Return the filter paper to the flask and determine the nitrogen, which is that of the albumoses.

Albumoses at 70° C.—Use a 50 cc aliquot of the coagulated nitrogen filtrate and proceed as in the case of proteoses in the cold. After completely saturating with zinc sulphate heat at 70° C. for 10 minutes, allow to stand overnight, and proceed as above.

Peptones, tannin and salt method.—Transfer a 50 cc aliquot of the coagulated nitrogen filtrate to a 100 cc flask. Add 15 grams of sodium chlorid and shake to dissolve as much of the salt as possible. Place the flask in the ice box at 15° C. A flask of distilled water and a second flask containing the tannin solution to be used are simultaneously placed in the ice box. The tannin solution is made by dissolving 24 grams of pure tannic acid in 76 cc of water and filtering. After standing for one hour in the ice box, 30 cc of the cold 24 per cent tannic-acid solution are added, then cold distilled water up to the mark, and the contents of the flask well mixed. After standing in the ice box over night the solution is filtered into a 50 cc flask at ice-box temperature and the nitrogen determined in the 50 cc of the filtrate. As the tannin used may contain nitrogen it is advisable to run a blank. Determine the nitrogen in 50 cc of the blank filtrate. The nitrogen in the 50 cc of the tannin-salt filtrate, after subtracting that found in the 50 cc filtrate of the blank determination, multiplied by two gives the amido nitrogen. The total nitrogen minus (amido nitrogen plus insoluble and coagulated nitrogen) gives the albumose and peptone nitrogen. The peptone nitrogen is obtained by deducting from the above figure the amount of nitrogen in the zinc-sulphate precipitate.

Report results as follows, using the amount of nitrogen found by the albumose method at room temperature when calculating the peptone nitrogen:

	Per cent.
Total nitrogen	.....
Insoluble and coagulable nitrogen	.....
Albumose nitrogen	.....
Albumose nitrogen at 70° C	.....
Peptone nitrogen	.....
Amido nitrogen	.....

The results reported by the cooperating chemists are given in the following table:

Nitrogen determinations on sample of commercial meat extract.

Analyst.	Acidity.	Nitrogen.				
		Insoluble and coagulable.	Albumose at 70° C.	Albumose at room temperature.	Peptone.	Amido.
	cc tenth-normal alkali per 100 grams.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Leavenworth	751.0	0.080	2.14	2.18	2.88	2.12
Jackson	641.0	.0852	.799	.728	6.896	.55
Cook	625.0	.203	2.18	2.10	3.06	2.90
Hanford	812.0	.168	1.15	1.83	1.60	4.66
Stookey	727.0	.24	1.39	1.40	1.10	5.53

Comment by the Referee.

The results show a fair degree of uniformity, considering that variations were to be expected from the fact that a new method was being tried (the modified tannin-salt method). Furthermore, the proteid separation methods are of necessity far from

satisfactory, due to our ignorance of the nature of the proteid molecule and the close relationship of its various hydrolytic products. The work is especially valuable for the criticism which it evoked and the comments by those cooperating and also by some who sent in no analytical results.

The acidity determination as carried out by titration with tenth-normal alkali, using litmus as an indicator, has met with much criticism, the figures varying from 625 to 812 cc.

The referee is anxious to obtain a more satisfactory method, but the use of litmus seems to be the best procedure at present, as the end point with phenolphthalein is masked by the dark color of these solutions.

The insoluble and coagulable nitrogen figures show great variation, and it is probably advisable to use a definite volume of wash water, as incomplete washing gives high results and long-continued washing yields low results. The two determinations should be separated, as the coagulable proteid figure is an important one and should be given alone.

The results obtained with zinc sulphate at room temperature are fully as high as those obtained by heating to 70° C. for ten minutes, the duplicates agree better, and the process is simpler.

The tannin-salt method for the separation of proteoses and peptones from simpler amido bodies is a method not likely to yield good results on first trial. The solution employed for this determination was undoubtedly too concentrated, and better results would have been obtained with a more dilute solution. The method will be further tested by various chemists, and with more careful directions good results can undoubtedly be obtained.

In using the tannin-salt method the solution foams to an objectionable degree during the Kjeldahl digestion unless precautions are taken to prevent it. The procedure followed by T. C. Trescot, of the Bureau of Chemistry, is to transfer 50 cc of the tannin-salt filtrate to a Kjeldahl digestion flask and add a few drops of sulphuric acid. Place the flask in the steam bath, connect with the vacuum, and evaporate to dryness. In the digestion process about 30 cc of sulphuric acid are added but no potassium sulphate. The large amount of sodium chlorid used in the process forms sufficient sodium sulphate, which acts in the same way as the potassium sulphate. The remainder of the process is carried out in the usual manner, and with the above modifications there is no difficulty in using the tannin-salt method in connection with the Kjeldahl digestion.

Comments by Analysts.

H. S. Grindley, of Urbana, Ill., says: "The method suggested for the determination of the acidity is very unsatisfactory. The determination of the insoluble and coagulable proteid in such a sample we find difficult because of the slow filtering. I think, also, that the quantity of sample taken for the determination of the secondary proteids by tannin salt is too large to give accurate results."

H. C. Bradley, of Madison, Wis., criticises the method as tedious. The litmus-acidity method is unsatisfactory, and he suggests that the acidity be determined in a separate sample, using a very dilute solution and phenolphthalein as indicator. He asks if in the determination of the various kinds of nitrogen present there is any significant gain made. Mr. Bradley suggests that we determine the more definite constituents of muscle, namely, creatin, creatinin, and xanthin bases.

E. E. Smith, of New York City, writes that the neutral point as obtained with litmus paper is inexact and that slow filtration of the insoluble and coagulable proteid is due in part to excessive acidity and in part to the attempt to filter cold. The 10 cc of tenth-normal acid added he considers excessive, as there is so little proteid present. Half saturating with sodium chlorid, Mr. Smith says, would facilitate coagulation and preserve the sample. In regard to coagulation he claims that usually the best

results are obtained by the addition of some sodium chlorid, the application of heat to the boiling point while in a neutral condition, the addition of just a sufficient amount (which is variable) of acetic acid to cause the separation of the albuminous substances in a flocculent form, maintaining in a hot condition on the water bath for the complete and flocculent separation of the albuminous substances, and finally the filtration while hot and washing with hot water.

L. B. Mendel, of New Haven, Conn., writes that acidity might well be determined on a separate sample. In regard to the albumose determination and the washing with saturated zinc-sulphate solution Mr. Mendel suggests that the bumping in the Kjeldahl determination, due to zinc sulphate crystallizing out on the filter papers, might be avoided by washing with a zinc-sulphate solution not concentrated sufficiently to deposit crystals by surface evaporation. He suggests that the creatin and purin content be especially considered, as these are the factors which characterize the product as a meat product.

L. B. Stookey, of Los Angeles, Cal., considers the methods as a whole to be quite satisfactory, but thinks the quantities used too large to give the best results.

Holmes C. Jackson, of Albany, N. Y., suggests that we discard the litmus method and employ a physical method for the acidity test, or titrate in dilute solution, using phenolphthalein as indicator, and add potassium oxalate to counteract precipitated phosphates or ammoniacal disturbances. Mr. Jackson suggests that for more accurate work we reprecipitate the proteoses out of a moderately concentrated solution. He also considers that the supposition that 50 cc of the filtrate from the tannin-salt precipitate represents one-half of the nonprecipitable nitrogen is unwarranted in view of the heavy precipitate present, and instead of being one-half it is more nearly five-eighths of the liquid; the solution employed for the tannin-salt treatment is too concentrated and should be diluted.

Results Obtained by the Referee.

The following studies include work on coagulable proteids, proteoses, and the separation of organic and inorganic phosphorus.

COAGULABLE PROTEIDS.

A cold-water extraction of beef was made, the sample being filtered and neutralized to litmus before it was divided into aliquots. All volumes are of 70 cc.

Table 1.—*Amount of nitrogen precipitated from cold-water meat extract by varying amounts of acetic acid and time of boiling.*

Time of boiling.	Acetic acid added (tenth-normal).			
	5 cc.	10 cc.	15 cc.	20 cc.
	Gram.	*Gram.*	*Gram.*	*Gram.*
Just boiled	0.0011	0.00084	0.00084	0.00112
Two minutes	.00168	.00112	.00084	.00084
Four minutes		.00168	.00112	.00112

Two pounds of lean beef were heated at 50° C. for two hours, ground and pressed, diluted, filtered, neutralized to litmus, refiltered, and aliquots taken. In cases where more than 5 cc of tenth-normal acid were added (10, 15, and 20 cc) the solutions did not coagulate thoroughly and filtration was impossible. With the addition of 5 cc of tenth-normal acetic acid the following results were obtained: Just boiled, 0.0578 gram; boiled two minutes, 0.0575 gram; boiled four minutes, 0.0589 gram.

A cold-water extraction of another sample of meat was prepared and neutralized to litmus before dividing into aliquots as before, the volumes, however, being made up to 60 cc. The following results were obtained:

TABLE 2.—*Nitrogen precipitated from a cold-water extract of meat under varying conditions.*

Time of boiling.	Neutral reaction.	Tenth-normal acetic acid.	
		2 cc.	10 cc.
	Gram.	*Gram.*	*Gram.*
Just boiled	0.0168	0.0236	0.0260
Two minutes	.0146	.0246	.0261
Four minutes	.0156	.0240	.0293

It is evident from these data that neutral solutions are not favorable to coagulation, as is well known, and that an excess of acid prevents coagulation. The time of boiling affects the results and it appears that the boiling should be continued for two minutes at least in order to insure complete coagulation.

A cold-water extraction of quail was used for the next study. Thirty grams of quail meat were shaken with cold water, washed until the filtrate was clear, and made up to 500 cc after filtering. All aliquots were made up to 70 cc with water. Two 50 cc aliquots of the original solution were diluted to 70 cc with water and coagulated by boiling two minutes. The acidity was due to the natural acid of the fresh meat juice, amounting to 1.45 cc of tenth-normal alkali per gram or 4.35 cc tenth-normal acid per 50 cc aliquot. The results are given as No. 9 and No. 10. The remaining 400 cc of the original solution were neutralized to phenolphthalein, made up to 440 cc volume and divided into eight 55 cc aliquots. All solutions were boiled two minutes.

TABLE 3.—*Nitrogen precipitated from cold-water extract of quail, using varying amounts of acetic acid (filtered before neutralizing).*

Sample.	Tenth-normal acetic acid.	Nitrogen precipitated.	Description of filtrate.
	Cc.	*Gram.*	
1	2	0.0146	Faintly turbid.
2	2	.0148	Do.
3	5	.0149	Clear.
4	5	.0149	Do.
5	10	.0079	Turbid.
6	10	.0079	Do.
7	15	.0039	Faintly turbid.
8	15	.0045	Do.
9	.....	.0143	Slightly cloudy.
10	.....	.0143	Do.

Four hundred cubic centimeters of a cold-water extract of quail meat, representing 30 grams of meat, were neutralized, filtered, and made up to 500 cc volume. This was divided into ten 50 cc aliquots. All solutions were boiled two minutes and the following results obtained.

TABLE 4.—*Nitrogen precipitated from cold-water extract of quail, using varying amounts of acetic acid (neutralized before filtering).*

Sample.	Tenth-normal acetic acid.	Nitrogen precipitated.	Description of filtrate.
	Cc.	*Gram.*	
1	0	0.0146	Turbid.
2	0	.0118	Do.
3	5	.0202	Faintly turbid.
4	5	.0194	Do.
5	10	.0205	Clear.
6	10	.0210	Do.
7	15	.0210	Do.
8	15	.0199	Do.
9	20	.....	Solutions discarded as turbid and filtered slowly.
10	20	.....	

In Table 4 the quail juice used was neutralized before filtering and consequently the acid albumin in this case was removed. In Table 3 the filtration was carried out before neutralizing and the acid albumin consequently remained in the filtrate. The results in Table 4 are higher than those in Table 3, and as each solution in both Tables 3 and 4 represents the same amount of soluble nitrogenous bodies the figures are interesting. It appears that after the acid albumin has been removed the added acid is left free to act with the salts in solution and the heat employed on the proteid matter which is in the coagulable form. In the cases of No. 9 and No. 10 of Table 3, where the natural acidity of the meat is unaltered, lower results are obtained than any of Table 4 except No. 2, in which case some error is evident. The amount of salts present is the same in all cases, and the results can not be ascribed to their influence. In Table 3, where 5 cc of acetic acid were added, the results are best, as a clear filtrate is indispensable. In Table 4, 5 cc of acid yield a turbid filtrate and 10 cc are necessary to give a clear filtrate, while 10 cc in Table 3 give a turbid filtrate.

That solutions of muscle proteids are rendered acid by coagulation has been thoroughly demonstrated by G. N. Stewart.[a] A factor secondary to the reaction is the salt content of the solution. Many workers have demonstrated that an albumin solution, whose salts have been removed by dialysis, will not coagulate, but on adding acid a soluble acid albumin may be formed, which on continued boiling is likely to be changed to an albumose. A good plan seems to be the one suggested by Cohnheim,[b] and recommended by E. E. Smith in this report, namely, the addition of sodium chlorid or some other neutral salt to the neutral solution to be coagulated and then a varying amount of acetic acid. It is essential to keep the reaction of the solution as slightly acid as possible, or to add a large amount of salt to insure complete coagulation and to hinder the formation of acid or alkali albumins. It seems doubtful if any universal rule for the coagulation of proteids can be framed. The proteids obtained from different sources are so diverse, and animal proteids themselves differ so much, that it seems necessary to treat each sample individually and so adjust the conditions to each sample as to give the maximum coagulation and a clear filtrate.

PROTEOSE RESULTS AT ROOM TEMPERATURE AND AT 70° C.

In all cases a neutralized filtered aliquot of the filtrate obtained from the determination of coagulable proteids was employed in this study. To this were added 3 drops of sulphuric acid, and the solution was then saturated with zinc sulphate. The determinations at 70° C. were saturated as is the usual custom and the saturated solution

[a] J. Physiol., 1899, *24:* 450.
[b] Zts. physiol. Chem., 1901, *33:* 455.

heated to 70° C. for ten minutes, then allowed to stand overnight. Solutions of meat extracts and water-soluble portions of beef and quail were used in making the following determinations:

TABLE 5.—*Comparison of proteose results at room temperature and at 70° C.*

Serial No.	Nitrogen precipitated.		Serial No.	Nitrogen precipitated.	
	At room temperature.	At 70° C.		At room temperature.	At 70° C.
	Gram.	*Gram.*		*Gram.*	*Gram.*
1813	0.02723	0.0275	17072	0.0994	0.0982
18372	.07916	.08562	17599 (*a*)	.00168	.00196
18634	.08309	.08224	17599 (*b*)		.00168
15416	.1124	.1075	17600 (*a*)	.00116	.00116
18609	.0160	.0138	17600 (*b*)		.00087

The above results are indecisive as to which method gives higher results. In all cases the differences are slight, and as the room temperature method gives better duplicates and is simpler it seems desirable to follow that procedure.

SEPARATION OF ORGANIC AND INORGANIC PHOSPHORUS.

Two methods were applied to meat extracts for separating these two forms of phosphorus, namely, the Siegfried-Singewald[a] method and the modified method of Hart and Andrews.[b] The latter could not be successfully applied to meat extracts, as the molybdic acid caused a heavy precipitate of the proteid bodies.

Organic phosphorus determinations by the Siegfried-Singewald method.

[Grams per 10 cc.]

Total phosphoric acid.	Organic phosphoric acid.	Organic phosphoric acid in presence of added sodium phosphate.
0.0117	0.0017	0.0023
.0140	.0017	.0016

To another sample 40 cc of a lecithin solution, containing 0.0005 gram of phosphoric acid per 10 cc were added, and the Siegfried-Singewald method applied. After deducting the amount of organic phosphorus which was added, the results show 0.0035 gram of phosphoric acid in the organic form per 10 cc, as compared with 0.0017 gram when no phosphorus was added. From the few results given above and the application of this method to some thirty samples of commercial meat extracts, it is the referee's opinion that the method does not effect a separation of the organic from the inorganic phosphorus.

Siegfried's method was also compared with the ordinary ether and alcohol extraction method for organic phosphorus. By the former method 0.16 per cent of phosphoric acid was found in organic combination in a solution of meat extract, and by the latter method 0.08 per cent. In all cases total phosphoric acid was determined by Neumann's[c] method. It is intended to investigate during the coming year the ether and alcohol extraction method for organic phosphorus determination.

[a] Zts. Nahr. Genussm., 1905, *10:* 522.
[b] Amer. Chem. J., 1903, *30:* 482.
[c] Zts. physiol. Chem., 1902, *37:* 115.

Conclusions and Outline of Work.

It seems advisable to give the question of the acidity determination in meat extracts and related products further study and to ask for cooperation on this point another year. The coagulable proteids should be determined separately from the insoluble proteids. The best conditions for the determination of coagulable proteids will be further studied. It appears that the individual factor is so great that it may be impossible to formulate a general method applicable to all meat products. The amount of water used in washing the insoluble proteid matter should be definitely stated.

The method of determining albumoses by heating to 70° C. for ten minutes after saturating with zinc sulphate gives no higher results than the method of saturating with zinc sulphate at room temperature. The room temperature method is simpler and gives better duplicates.

No satisfactory conclusion can be reached in regard to the application of the tannin-salt method, as herein outlined, from the limited number of cooperative results obtained. With more complete directions and the use of a more dilute solution better results might have been obtained by the various collaborators. The method needs further study and trial in the hands of experienced workers. The creatinin determination, as well as the question of organic phosphorus separation, should be taken up by the referee in 1907.

REPORT ON DAIRY PRODUCTS.

By F. W. Woll, *Referee.*

The referee was requested, by vote of the association last year, to continue the study of the preservation of milk samples for the determination of milk proteids, and to take up two new subjects for study, namely, methods of determining sugar in condensed milk, dried milks, or milk powders, and, second, methods of detecting the adulteration of butter with small quantities of foreign fats.

In view of the fact that the first subject mentioned can only be satisfactorily worked out by individual effort, as is indicated by the small interest taken in the subject by our chemists in the past, and furthermore because experience has shown that the cooperative work done stands in nearly inverse ratio to the amount outlined for study, your referee decided to request the cooperation of chemists in a study of only two subjects:

(1) The analysis of condensed milk, including determinations of sugar and fat, and

(2) The Gottlieb method of determining fat in skim milk and other dairy products.

By arrangement with the associate referee on adulteration of dairy products, Mr. Leach, the third subject recommended by the association for cooperative work, methods of detecting adulteration of butter with small amounts of foreign fats, was left to be studied by him, if practicable, as properly coming under his domain.

Sixteen different chemists signified their willingness to cooperate in the work outlined by the referee, and two carefully prepared samples of condensed milk, sweetened and unsweetened, were furnished them, the following explanatory letter having been previously mailed:

Madison, Wis., *March 27, 1906.*

Dear Sir: The cooperative work on dairy products for the Association of Official Agricultural Chemists during this year was outlined in my circular letter of the 3d inst.

With reference to I a (Effect of preservatives upon the determination of albumin in milk), I would say that I was not present at the last two conventions of the association and do not possess sufficient information in regard to the results of the work so far accomplished to outline further work on this subject. Chemists who are so situated as to be able to continue this work are urged to do so; when the proceedings of last year's convention are published, it is likely that the direction will be shown in which further study of the subject should go.

As to I b and II b (Methods of determining sugar and fat in condensed milk), samples of unsweetened condensed milk will be sent about April 15 to all chemists who have signified their intention to cooperate in this work. You are requested to make the following determinations:

Sugar.—In the sample of sweetened condensed milk, (1) gravimetric or volumetric method with Fehling solution, and (2) polariscope method, both before and after inversion with citric acid or yeast; direct gravimetric and polariscope methods in the sample of unsweetened condensed milk.

Fat.—(1) The Babcock asbestos method. Five grams of a 40 per cent solution of condensed milk in water are weighed into a copper asbestos tube and after drying extracted for five hours, as in case of cow's milk. On completed extraction, the tubes are placed in distilled water to dissolve the sugar, then dried and extracted for another five hours, when the fat is dried and weighed.

(2) The modification of the Babcock centrifugal method by Leach (Food Inspection, p. 149) or by Farrington (Wisconsin Seventeenth Annual Report 1900, p. 86) may be used in the case of sweetened condensed milk and the direct Babcock centrifugal method in case of the unsweetened milk.

(3) The Gottlieb method (see below).

It is requested that, if practicable, comparative analyses by these methods of other samples of condensed milk and of dried milk or milk powders be made and reported.

As to II a (Comparisons of the official and the Gottlieb methods for the determination of fat in skim milk and buttermilk), chemists are asked to make comparative fat determinations in a number of samples of skim milk and buttermilk by these two methods.

The Gottlieb method was originally described in Landw. Versuchs.- Stat., 1892, *40:* 1–27. It is now the official method in Sweden and Denmark for the determination of fat in skim milk and buttermilk, recent work by European chemists having shown that the ordinary extraction methods give too low results for milks low in fat. The Gottlieb method is as follows:

"Ten cc of milk are measured into a glass cylinder three-fourths inch in diameter and about 14 inches long (a 100 cc burette or a eudiometer tube will do); 1 cc concentrated ammonia is added and mixed thoroughly with the milk; the following chemicals are next added in the order given: 10 cc of 92 per cent alcohol, 25 cc of washed ether and 25 cc of petroleum ether (boiling point below 80° C.), the cylinder being closed with a moistened cork stopper and the contents shaken several times after the addition of each. The cylinder is then left standing for six hours or more. The clear fat solution is next pipetted off into a small weighed flask by means of a siphon drawn to a fine point (see fig. 6, Landw. Versuchs.-Stat., *40:* 6), which is lowered into the fat solution to within 0.5 cm of the turbid bottom layer. After evaporating the ether solution in a hood the flasks are dried in a steam oven for two to three hours and weighed. This method is applicable to new milk, skim milk, buttermilk, whey, cream, cheese, condensed milk, and milk powder, but has been found of special value for determining fat in skim milk, buttermilk, cheese, and condensed milk. In the case of products high in fat a second treatment with 10 cc each of ether and petroleum ether is advisable in order to recover the last trace of fat."

It is requested that reports of the work done along the preceding lines of study be sent to the referee as soon as finished, so as to render possible further investigation of points that may suggest themselves. All reports should be in by October 1. I shall be pleased to correspond with chemists who need additional information in regard to the work outlined above.

Hoping that you may be able to contribute in some measure to the further advancement of our knowledge of the subjects scheduled for study, I am,

Very respectfully, yours,

F. W. Woll,
Referee on Dairy Products.

Reports of the work done on these samples were received from seven chemists, located at four different stations,[a] the results being given in the following pages. For the sake of convenience the analyses and the discussion of the results are arranged under four headings: (1) Sugar in condensed milk. (2) Fat in condensed milk. (3) Fat in dried milk and milk powders. (4) The Gottlieb method of fat determination.

[a] Results obtained by the Dairy Laboratory, Bureau of Chemistry, U. S. Department of Agriculture, were received after this report was written and have been included in the tables given below.

(1) *Sugar in condensed milk.*—The following results were obtained for sugar in condensed milk by the different methods:

Percentage of sugar in condensed milk by different methods—referee's samples.

Analyst.	Gravimetric method.		Polariscopic method.	
	Lactose.	Sucrose.	Lactose.	Sucrose.
Sample A, sweetened condensed milk:				
Fulton, Massachusetts	13.37	40.62	.....	.....
Norton, Arkansas	9.5	45.48	.....	.....
Bartlett, Maine	14.94	40.18	.....	.....
Jaffa and Stewart, California	14.37	41.78	10.88	40.90
Olson, Wisconsin	14.69	35.25	.....	38.67
Sample B, unsweetened condensed milk:				
Fulton, Massachusetts	10.49	.....	.....	.....
Norton, Arkansas	9.4	.....	11.3	.....
Bartlett, Maine	10.08	.....	.....	.....
Olson, Wisconsin	11.05	.....	11.56	.....
Patrick and Boyle, Washington, D. C.	10.04	.....	10.07	.....

Other determinations were made on one sample of sweetened condensed milk and four samples of unsweetened condensed milk at the California and Wisconsin Experiment stations, as shown below.[a]

Other determinations of sugar in condensed milk.

Analyst.	Gravimetric.		Polariscope.	
	Lactose.	Sucrose.	Lactose.	Sucrose.
Sweetened condensed milk:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Olson, Wisconsin	16.41	35.91	.....	34.25
Unsweetened condensed milk:				
Jaffa and Stewart, California	9.28	.....	9.36	.....
Olson, Wisconsin	9.91	.....	9.19	.....
Jaffa and Stewart, California	8.11	.....	8.00	.....
	10.87	.....	10.74	.....
	9.96	.....	9.84	.....

REMARKS BY ANALYSTS.

Massachusetts.—Solutions were prepared by diluting 200 grams to 500 cc. It is impossible to prepare sample B satisfactorily because of the churned condition of the fat and of the action of the formalin, which was present in considerable quantity. Having no polariscope in condition, the sugar results were obtained by gravimetric methods.

Maine.—The solution of condensed milk was boiled with the copper solution for two minutes.

California.—The discrepancy between the determinations of lactose by the polariscope and by the Fehling solution I can only account for on the ground that some of the cane sugar had been inverted or reduced at the time of manufacture. All of the determinations were made in duplicate. The analysis of sample A calculated to normal milk by use of either the "solids-not-fat" method, or on the basis of 0.70 per cent ash, gives a possible milk, if we use the polarimetric determination of lactose of 10.88 per cent, as follows: Moisture 86.67 per cent, protein 3.38 per cent, fat 4.37 per cent, sugar 4.88 per cent, and ash 0.70 per cent. The results are not satisfactory, however, if we use the figure 14.78 per cent. The determinations of lactose by the gravimetric method were made by weighing the cuprous oxid.

Wisconsin.—Twenty cubic centimeters of a 40 per cent solution of condensed milk were treated with 0.25 gram of citric acid, made up to 200 cc, filtered, and 20 cc of the

[a] See also report of Messrs. G. E. Patrick and M. Boyle, p. 106.

filtrate were added to the boiling Fehling solution and boiled for six minutes. The cuprous oxid was collected and washed on the filter, and weighed after reduction to cupric oxid. After correction for volume and the amount of copper in CuO, the equivalent in lactose was obtained from the table in Bulletin 46 of the Bureau of Chemistry and the per cent of lactose in the condensed milk calculated.

For the sweetened condensed milk 100 cc of the filtrate were treated with 1 gram of citric acid for inversion and neutralized with sodium carbonate, then boiled to precipitate the albumen, filtered, and made up to 100 cc. Ten cubic centimeters of the filtrate were taken for quantitative determinations, and boiled with the Fehling solution for two minutes.

For the polariscopic method 26.048 grams were treated with 0.5 gram of citric acid, neutralized with sodium carbonate, boiled ten minutes, made up to 200 cc, and filtered. The filtrate was polarized in 400 mm and 200 mm tubes. One hundred cubic centimeters of filtrate were inverted with 1 gram of citric acid, neutralized, cooled, and potassium mercuric iodid added, made up to 100 cc and filtered. This solution was polarized and the amount of sucrose after volume correction was calculated by the usual formula.

Of the samples of unsweetened condensed milk, 20.493 grams were treated with 0.5 gram of citric acid and neutralized, boiled for ten minutes, cooled, made up to 200 cc, and filtered. The filtrate was polarized in 400-mm tubes. After correction for volume was made the per cent of lactose in the milk was obtained.

DISCUSSION OF RESULTS.

The results for lactose in both sweetened and unsweetened condensed milk are fairly concordant, with one exception in each case. This can not, however, be said to be the case with the determinations of sucrose in the sweetened condensed milk. It is a question, however, how much the personal factor enters into the results. It has often been found in the past that unfamiliarity with the methods under investigation has been responsible for strange results on cooperative work. Detailed directions as to the manner of procedure were not sent out by the referee in the case of the condensed milk work, as it was felt that this year's work was only preliminary, and it was desired to obtain information as to the present methods of determining sugar in condensed milk in vogue among station and food chemists and the kind of results obtained. It is planned to continue this study next year, in the expectation that as satisfactory methods as possible for the determination of both lactose and sucrose in condensed milk may be worked out and adopted as official by the association.

(2) Fat in Condensed Milk.

Fat was determined in the condensed milk by seven analysts, located at five different stations, the Babcock asbestos method, the Babcock centrifugal method as modified by Leach or Farrington, or the Gottlieb method being used by the various chemists.

The following table shows the results obtained with these methods:

Percentage of fat in condensed-milk samples.

Analyst.	Asbestos method.			Babcock test.		Gottlieb method.
	Extraction 1.	Extraction 2.	Total.	Leach.	Farrington.	
Referee's sample A, sweetened condensed milk:						
Smith, Massachusetts	2.25	6.09	8.34	.....	.....	7.97
Whittier, Massachusetts	2.43	5.82	8.25	.....	.....	.....
Fulton, Massachusetts	.....	.....	.....	9.0	8.58	.....
Norton, Arkansas	.....	.....	.....	8.4	.....	[a] 4.70
Bartlett, Maine	.....	.....	8.76	.....	8.7	8.81
Olson, Wisconsin	3.18	5.08	8.26	9.08	8.8	8.13
Jaffa and Stewart, California	.....	.....	9.92	9.75	.....	.....
Referee's sample B, unsweetened condensed milk:						
Smith, Massachusetts	6.84	.45	7.29	.....	.....	7.12
Whittier, Massachusetts	6.86	.42	7.28	.....	[b] 6.48	.....
Norton, Arkansas	.....	.....	.....	.....	[b] 6.9	[a] 4.9
Bartlett, Maine	.....	.....	7.34	.....	[b] 5.93	7.03
Olson, Wisconsin	7.20	.02	7.22	6.90	7.7 / [b] 6.8	7.09
Patrick and Boyle	.....	.....	[c] 7.55	.....	.....	[a] 7.24
Other samples of sweetened condensed milk:						
Olson, Wisconsin	5.78 / 7.56	2.26 / 2.09	8.04 / 9.65	.....	.....	8.37 / 9.66
Jaffa and Stewart, California	.....	.....	9.70	.....	9.30	.....
Other samples of unsweetened condensed milk:						
Olson, Wisconsin	7.24 / 8.08	.08 / .60	7.32 / 8.68	.....	.....	7.53 / 8.93
Jaffa and Stewart, California	.....	.....	7.20	6.70	.....	.....

Averages of comparative determinations.

Method.	Sweetened.	Unsweetened.
	Per cent.	*Per cent.*
By extraction method	[d] 8.61	[d] 7.55
Gottlieb method	[d] 8.59	[d] 7.54
By extraction method	[e] 9.29	[f] 7.21
Babcock test, Leach modification	[e] 9.38	[f] 6.80
By extraction method	[f] 8.51	[e] 7.28
Babcock test (original)	[f] [g] 8.75	[e] 6.40

[a] Extracted only once.
[b] Babcock original method.
[c] Adams method. See p. 106.
[d] Five determinations.
[e] Three determinations.
[f] Two determinations.
[g] Farrington modification.

REMARKS BY ANALYSTS.

Massachusetts.—In using the Babcock asbestos method it would seem advisable to continue the first extraction over night, as in the case of feedstuffs, then proceed as stated.

In the centrifugal method the decanting and pipetting processes, as outlined for the modified Babcock methods, did not prove entirely satisfactory, therefore the solutions were decanted through parchment filter paper (to prevent loss) and the detached particles returned to the test bottles. Fifteen cubic centimeters of the diluted samples were used in the several tests. The Leach modification gave slightly higher results than the Farrington on the sweetened product. The hardening action of the formaldehyde was very apparent in the unsweetened sample. Comparatively few of the separations could be considered perfect tests.

The Gottlieb method seems rather more applicable to materials of a low fat content and with such samples blank determinations are evidently necessary. Closed cylindrical separatory funnels should facilitate the process materially.

Maine.—Could not make the Babcock centrifugal method come up to the others on sample B. In the asbestos method two extractions were made, but the fat was not weighed after the first extractions were completed. The sweetened sample was extracted, then soaked in water as directed, dried, and extracted again. The unsweetened sample was not treated with water.

California.—The extractions of fat were made in S. & S. thimbles.

Wisconsin.—After the first extractions in the Babcock asbestos method, the cylinders were allowed to soak in a liter of distilled water for about three hours. They were then rinsed with distilled water and dried in a steam oven at 92° C. for five hours before the second extraction was commenced. The first extraction was continued overnight and the second for about eight hours.

For simplicity and accuracy the Gottlieb method, in our experience, is to be preferred to the extraction method, especially for skim milk, buttermilk, and milks low in fat. It also appears to give most satisfactory results for fat in condensed milk and cheese.

DISCUSSION OF RESULTS.

While the results obtained by the various analysts are not always as concordant as might be desired, some facts are nevertheless brought out in a striking manner. First, the necessity of a double extraction in the ether-extraction method. In the sweetened condensed milk two-thirds or more of the fat may escape extraction when extracted only once, even if the process be continued for twelve hours or more. In unsweetened condensed milk the error introduced by making a single extraction only is, as a rule, small, but even here the safer way is to make a second extraction, after treating the extraction tubes with water and drying. If this modification is introduced in the asbestos method, it may safely be made official for fat in condensed milk. The Babcock centrifugal method, modified by Leach, which is the only method now given in Bulletin 65 of the Bureau of Chemistry, is provisional only, and may be depended upon to give satisfactory and correct results when the directions are followed in detail, but it would seem that with it, as the official method of the association, the gravimetric ether-extraction method should be given, modified to provide for double extraction with intervening removal of the sugar so as to insure complete recovery of the entire fat content of the condensed milk.

Either of the modifications of Babcock's centrifugal method appears to give satisfactory results, there being but slight differences in the averages of several determinations by the double-extraction method and the Leach or Farrington modifications. The average results obtained by the Gottlieb method and by double extraction are almost identical. In the former method the solution should be treated a second time with 10 cc of sulphuric and petrolic ether, in the case of condensed milk, as with all other dairy products containing more than a fraction of a per cent of fat, to allow for the error of not pipetting off the entire volume of the fat solution, and for the fat adhering to the side of the burette on drawing off the fat solution. The original Babcock test is not applicable even for unsweetened condensed milk, as the results, if they can be read at all, are likely to be about 1 per cent or more too low (average of three different determinations, by double extraction, 7.28 per cent; by original Babcock test, 6.40 per cent).

(3) Fat in Dried Milk and Milk Powders.

Only a few analyses of these products were made, all in the laboratory of the Wisconsin station. The results are presented in the following table:

Fat in dried milk and milk powders, determined by two methods.

Material.	Ether extraction.	Gottlieb.	Difference.
	Per cent.	*Per cent.*	*Per cent.*
Milk flakes	0.31	0.80	+0.49
Nutrium	.52	1.74	+1.22
Milcora	.35	2.19	+1.84
Cream flakes	17.04	17.32	+ .28
Creamora	29.13	31.66	+2.53
Tru-milk	7.75	8.41	+ .66
Tru-cream	25.37	27.43	+2.06
Average	11.49	12.79	+1.30

Incomplete as the investigation is, the results obtained show plainly that the ordinary ether extraction of fat in dried milks give lower results than the Gottlieb method, the differences ranging from about 0.5 per cent to 2.5 per cent in dried milks high in fats, with an average difference of 1.30 per cent in favor of the Gottlieb method. The accuracy of the results obtained by the Gottlieb method will be discussed under the following heading.

(4) Results with the Gottlieb Method.

No reports of work with this method, aside from the results already presented with condensed milk, were received by your referee. In our own laboratory a number of samples of skim milk, buttermilk, and cheese were analyzed during the early part of the year by G. von Ellbrecht and George A. Olson, comparative determinations being made by the official asbestos extraction method, the Gottlieb method, and in some cases by the Babcock centrifugal method. The results of these determinations are given below.

Comparison of fat determinations made on different materials by three methods (Wisconsin).

Material.	Method.		
	Extraction.	Gottlieb.	Babcock.
	Per cent.	*Per cent.*	*Per cent.*
Separator skim milk	0.091	0.143	Trace.
	.046	.133	0.02
	.155	.192	.02
Average	.097	.152	.02
Buttermilk [a]	.133	.403	.12
	.153	.347	.11
	.190	.379	.04
Average	.159	.376	.09
New milk	3.85	3.95	.....
	3.81	3.82	.....
	4.61	4.74	.....
Average	4.09	4.14	.....
Cheese	36.10	36.50	.....
	37.20	37.32	.....
	35.11	36.75	.....
Average	36.14	36.86	.....

[a] A sample of buttermilk analyzed at the California station gave the following results: Extraction method, 0.85 per cent, Gottlieb method, 0.90 per cent; Babcock test, 0.75 per cent.

In the analysis of cheese by the Gottlieb method 1 cc of hydrochloric acid and 9 cc of water were added to about 2 grams of cheese and the mixture heated until a uniform emulsion was obtained. This was then treated with 10 cc of alcohol and 25 cc each of sulphuric and petrolic ether, shaking thoroughly after each addition, as in the case of milk. The official gravimetric method for fat in cheese gave, on the average, 0.72 per cent lower results than the Gottlieb method modified to this extent that hydrochloric acid instead of ammonium hydroxid was used for bringing the cheese into an emulsion, a modification that has been adopted by many European chemists.

The Gottlieb method is, as stated in the directions for cooperative work, especially adapted for the analysis of milk low in fat, like skim milk and buttermilk. A large amount of analytical work has been done with the method in Europe during the last two years which shows conclusively that it gives correct results and that the fat obtained by this method is pure butter fat. It follows, therefore, that all the fat is not obtained in our official ether-extraction method or methods, apparently because the fat is protected by a layer of sugar or nitrogenous substances, or both, which is formed in drying the milk. On this point it is only necessary to refer to recent publications on the subject of milk analysis, especially to T. S. Thomsen's [a] work, showing that when milk proteids are peptonized prior to extraction there is no difficulty in reaching as high results by extraction as by the Gottlieb method. (See also the following paper by George A. Olson, on the examination of the fat obtained by the two methods). A similar single experiment in our laboratory with a sample of condensed milk gave 9.66 per cent of fat by ether-extraction and 9.94 per cent by the official method after digesting with one-tenth of a gram of pepsin per 250 cc of a 40 per cent solution for several days (doubtless longer than was necessary)—i. e., practically the same result as obtained in the Gottlieb method. For the reasons stated, the referee would recommend that the Gottlieb method be made provisional for the analysis of fat in milk.

The referee has been instructed by a unanimous vote of the Committee on Revision of Methods to recommend that the conversion factor for protein in milk be changed to 6.38, which is the factor now quite generally used by dairy chemists in this country and abroad. All who are at all familiar with the literature on the subject know that it is wrong to apply the factor 6.25 to dairy products, and this factor has been abandoned by most chemists doing work in this line. It has been allowed to remain in our methods only through conservatism, or through an oversight, because nobody has interested himself in having it corrected. The referee would recommend, therefore, that the factor be changed to that adopted by English chemists, 6.38; 6.37 or 6.40 would be equally acceptable, were it not desirable to have methods and statements of analysis always uniform in different countries, so far as possible, where this can be attained without sacrificing accuracy of results.

Recommendations.

It is recommended that—

(1) The following method of extraction be adopted as provisional for the determination of fat in condensed milk:

Fat.—Extract the solid residue of about 5 grams of a 40 per cent solution of the condensed milk with ether in the usual manner, dry, leave tubes in the dish containing about a liter of water for two or three hours, extract again for about five hours, and determine fat as under milk. (Bulletin 46, page 54.)

(2) The Gottlieb method be made provisional, the following directions to be included under determination of fat in milk:

Place about 10 grams of the milk in a 100 cc burette or eudiometer tube, add 1 cc of concentrated ammonium hydroxid and mix thoroughly. Add the following chemicals in the order given: 10 cc of 92 per cent alcohol, 25 cc of washed ether, and 25 cc of petroleum ether of a boiling point below 80° C, closing the cylinder with

[a] Mælkeritidende, 1905, *18:* 359–365; Exper. Stat. Record., 1906, *17:* 437.

a moist cork stopper and shaking the contents several times after each addition. Leave for six hours or more; pipette off the clear fat solution into a small weighed flask by means of a siphon drawn to a fine point, which is lowered into the fat solution to within 0.5 cm of the turbid bottom layer. Evaporate the ether solution in a hood, dry in a steam oven for two to three hours and weigh. In the case of new milk and dairy products high in fat treat with a second amount of 10 cc each of sulphuric and petrolic ether to recover the last traces of fat.

(3) The conversion factor for protein in milk and dairy products be changed to 6.38 throughout the methods.

(4) The study of methods of analysis of condensed milk be continued, especially with reference to the determination of lactose and sucrose in the sweetened product.

SUBREPORT ON ANALYSIS OF DAIRY PRODUCTS.

By G. E. Patrick and M. Boyle.

With four of the five samples of unsweetened condensed milk, reported in the following table, one extraction by the Gottlieb-Roese method gave results a trifle higher than did two extractions (with intermediate extraction with water) by the Adams paper coil [a] method—and 0.2 to 0.25 per cent higher than by a single extraction by that method. With one of the five samples—referee's sample No. 2930—the result was quite different; a single extraction by the Gottlieb-Roese gave 0.2 per cent less than was obtained by even one extraction by the Adams. For this variation we have no explanation at present. Forty per cent solutions of the samples were used for analysis.

Fat determined in unsweetened condensed milk by two methods.

Sample.	Adams method.		Gottlieb-Roese method, one extraction.
	One extraction, 20 to 30 hours.	Two extractions, with intermediate soaking in water.	
No. 2930 (referee's sample):	*Per cent.*	*Per cent.*	*Per cent.*
a	7.44	7.55	7.26
b	7.52	7.61	7.17
c	7.43	7.50	7.24
d	.....	.....	7.29
Average	7.46	7.55	7.24
Second ether extract (gram)	.....	0.0019–0.0028	.....
No. 2528:			
a	7.69	7.86	7.90
b	7.68	.....	8.03
c	7.69	7.88	.....
Average	7.69	7.87	7.96
Second ether extract (gram)	.....	0.0052–0.0059	.....
No. 2530:			
a	9.42	9.64	9.57
b	9.31	9.54	9.68
c	9.35	9.55	9.68
d	.....	.....	9.54
e	.....	.....	9.58
f	.....	.....	9.66
Average	9.36	9.58	9.62
Second ether extract (gram)	.....	0.0065–0.0079	.....
No. 2610:			
a	8.22	8.29	8.47
b	8.20	8.36	8.40
c	8.24	8.39	.....
Average	8.22	8.35	8.43
Second ether extract (gram)	.....	0.0023–0.0049	.....

[a] Analyst, 1885, *10:* 46.

Fat determined in unsweetened condensed milk by two methods—Continued.

Sample.	Adams method.		Gottlieb-Roese method, one extraction.
	One extraction, 20 to 30 hours.	Two extractions, with intermediate soaking in water.	
No. 2529:	*Per cent.*	*Per cent.*	*Per cent.*
a	6.94	7.00	[a] 7.12
b	6.95	7.06	[a] 7.17
c	6.87	6.99	.....
Average	6.92	7.02	7.14
Second ether extract (gram)	.....	0.0015–0.0022	.....

[a] In these two Gottlieb-Roese tests, 2 cc of water were added, and 2 cc more of alcohol than the directions require. It is possible that this change increased the result a trifle.

The referee's sample of sweetened condensed milk was lost by breakage in transit, but the following determinations were made on other milks:

Fat determinations in sweetened condensed milk by two methods.

Sample.	Adams method.		Gottlieb-Roese method, one extraction.
	One extraction, 20 to 30 hours.	Two extractions, with intermediate soaking in water.	
No. 2611:	*Per cent.*	*Per cent.*	*Per cent.*
a	8.66	8.83	8.72
b	8.85	9.05	8.74
c	8.70	8.96	.....
Average	8.74	8.95	8.73
Second ether extract (gram)	.....	0.0020–0.0031	.....
No. 2621:			
a	9.52	10.03	9.55
b	9.62	10.06	9.49
c	9.55	10.03	.....
Average	9.56	10.04	9.52
Second ether extract (gram)	.....	0.0050–0.0056	.....

These sweetened condensed milks were diluted with five times their weight of water, before testing by the Adams method, so that the amount of the original sample on an extraction paper was but little more than 1 gram. This high dilution magnifies errors seriously, and one variable error, that due to ether extract from the paper, is unavoidable. We have never been able to obtain a uniform ether extract from blank papers, the range being from 1 to 4 mg usually. In all of the work reported in this paper a deduction of 0.0018 gram for this error was made from the *first* extraction and none from the second. An error of 1 to 2 mg in the first or second extract, or in the two together, is easily possible from this source; and on such small charges of the original material even these small errors become of importance when expressed in percentage. Here, therefore, in the error due to the extract from the papers, is a serious fault of the Adams method, a fault which can be overlooked in ordinary milk analysis, but which assumes importance when the method is applied to condensed milks, especially the sweetened ones.

However, after making reasonable allowance for errors due to this cause, it appears from the above work on the two samples of sweetened condensed milk that *one* extraction by the Gottlieb-Roese method gave about the same results as did one extraction by the Adams method, and the query arises whether a second extraction by the Gott-

lieb-Roese would not have raised the results as much as did the second extraction by the Adams. Unfortunately this comparison was not made.

In carrying out the Adams method in this laboratory [Bureau of Chemistry] the milk, properly diluted if need be, is spread upon an S. & S. "fat-free" paper from a weighing pipette, the paper is allowed to become sensibly dry at room temperature, is then dried for ten to fifteen minutes in the oven at 100°, immediately rolled in a coil, with two very narrow strips of the same kind of paper between the layers (in place of the string proposed by Allen[a]), and extracted in a Knorr apparatus with water-free ether. This apparatus probably acts less rapidly than does the Soxhlet upon such material, and for this reason the time of extraction was extended to over twenty hours in the work here reported.

Fat determinations in buttermilk by two methods.

Sample.	Adams method.		Gottlieb-Rose method, one extraction.
	One extraction, 30 hours or more.	Two extractions, with intermediate soaking in water.	
No. 2937:	*Per cent.*	*Per cent.*	*Per cent.*
a	0.681	0.730	0.843
b	.724	.776	.841
c	.781	.830	.....
Average	.729	.779	.842
Second ether extract (gram)	.....	0.0020–0.0023	.....

This buttermilk is believed to have been produced by churning sour milk. It was diluted with an equal weight of water before treating by the Adams method. The Gottlieb-Roese method gave distinctly higher results than did the Adams, even with two extractions, and the results on the same sample agree better. The Babcock centrifugal method gave on this sample, in triplicate test, 0.80, 0.80, and 0.80.

One point observed in the working of the Gottlieb-Roese method seems worthy of mention. When the line between the mixed ethers and the watery liquid is not clear it can usually be made perfectly clear by adding a little sodium chlorid—0.1 to 0.3 gram suffices. It must be added *after* the two ethers have been added and shaken in, not before. Its effect is of course purely physical and perhaps any other salt would do as well.

Instead of the original Gottlieb tube, we have used with much satisfaction Röhrig's modification,[b] which is provided with a stopcock for drawing off the ethereal solution of fat. But the stopcock should be lower down on the tube than Röhrig advises—i. e., at the 22 or 23 cc rather than the 25 cc mark.

[a] Analyst, 1886, *11:* 72.

[b] A. Röhrig, Zts. Nahr. Genussm., 1905, *9*: 531.

Lactose determinations in unsweetened condensed milk.

Sample.	By copper reduction, Soxhlet method.	By polariscope, clarification by mercury: (acid $Hg(NO_3)_2$).
	Per cent.	*Per cent.*
No. 2930, referee's sample:		
a	10.01	
b	10.02	
c	10.06	10.07
d	10.06	
Average	10.04	
No. 2530:		
a	10.50	
b	10.50	
c	10.52	10.19
Average	10.51	
No. 2528:		
a	10.73	
b	10.65	
c	10.68	10.57
Average	10.69	
No. 2610:		
a	10.14	
b	10.15	
c	10.16	9.97
Average	10.15	
No. 2529:		
a	9.18	
b	9.17	
c	9.25	8.71
Average	9.20	
No. 2531:		
a	9.40	
b	9.37	
c	9.33	9.00
Average	9.37	

In the polariscope work, correction for the volume of the mercuric precipitate was made according to Leffman and Beam—weight of proteids multiplied by 0.8 and weight of fat by 1.075.

With five out of the six samples the results by the polariscope were lower than by copper reduction; in three cases the deficit was serious, ranging from 0.32 to 0.49 per cent. The results by copper reduction are believed to be the more trustworthy.

FAT DETERMINATIONS IN CHEESE BY THE GOTTLIEB AND THE ETHER-EXTRACTION METHODS.

By George A. Olson.

It is conceded that higher percentages of fat are generally obtained by the Gottlieb than by the present ether-extraction method. At the same time it has been questioned whether or not this increased per cent of fat is not due to some substance or substances other than fat, introduced by the chemicals used as solvents in the Gottlieb method or through their action.

A blank test of the chemicals used as solvents was first made and after evaporation and drying no increase in weight was obtained. Comparative examinations of the fat obtained by the Gottlieb and the ether-extraction methods were then made. Equal

quantities of a sample of old cheese were extracted by the two methods given, the fatty solution was evaporated, and the fat dried for eighteen hours at 92° C. The two preparations of fat had the following chemical and physical properties:

Determination of fat in cheese by the Gottlieb and the ether-extraction methods.

CHEMICAL EXAMINATION.

Test.	Gottlieb method.	Ether-extraction method.
Refractive index, 36° C	41	41.0
38° C	40	40.0
41° C	39	38.5
Specific gravity, 69° C	0.900	0.8995
Köttstorfer number	230.69	228.34
Butyric acid, per cent	5.04	5.04
Melting point [a], ° C	29.5	29.5

PHYSICAL EXAMINATION.

Gottlieb method.	Ether-extraction method.
Clear; medium dark color; solidified at room temperature (22° C.).	Cloudy; lighter color; not completely solidified.

[a] Wiley's method.

These results, which are the averages of several determinations, indicate such slight differences in the chemical and physical properties of the fat obtained by the two methods that it can not be definitely stated that the fats obtained by the two methods are not identical. Wider differences may be obtained in the fat from the same sample by either of the two methods of extraction. Since the two fats appear to be similar in nature and true butter fat, it follows that quantitative results obtained by the Gottlieb method show the true fat content of dairy products, and this is of especial importance in the case of milk or other dairy products containing only small amounts of fat.

DETERMINATION OF THE ACIDITY OF CHEESE.

By Alfred W. Bosworth.

In the official methods under cheese analysis a provisional method for the determination of the acidity of cheese is given, which reads as follows:

To 10 grams finely divided cheese add water, at a temperature of 40°, until the volume equals 105 cc; agitate vigorously and filter. Titrate portions of 25 cc of filtrate corresponding to 2.5 grams of cheese with standardized solution of sodium hydroxid, preferably one-tenth normal. Use phenolphthalein as indicator. Express amount of acid as lactic.

The following modification is proposed:

Extract 25 grams of finely divided cheese with 200 cc of water at 55° C., decant the supernatant liquid onto a cotton filter, and complete the extraction with successive portions of water until nearly 1 liter is collected. Make up to 1 liter, shake, and titrate 100 cc with twentieth-normal sodium hydroxid, using phenolphthalein as an indicator. The figure obtained is to be multiplied by 20, which will give the acidity of 100 grams of cheese expressed as tenth-normal alkali.

The lactic acid present in cheese was determined by grinding 5 grams of cheese with sand, extracting with water acidulated with sulphuric acid, and extracting the resulting solution with ether. A lactic acid determination in this ether extract gave

0.405 per cent. At the same time a water extract was prepared, as explained above, and a determination of lactic acid in it gave 0.410 per cent. This acid was in combination, and therefore the test for free lactic acid gave no results. As free lactic acid is never found in cheese, there seems to be no reason why the acidity should be expressed as lactic acid, as the official methods direct.

The lactic acid is present as calcium lactate. The bacteria present in the cheese produce lactic acid from the milk sugar. This lactic acid as developed splits off calcium from the calcium paracasein and the insoluble calcium phosphate, forming calcium lactate, soluble calcium phosphate, and free paracasein. The calcium lactate is neutral, and the free paracasein, being insoluble, does not affect the acidity as determined. It is the soluble calcium phosphate which causes the acidity.

Tables 1 and 2 show how the acidity of the cheese increases with the increase in solubility of the phosphoric acid. The acidity as given in these tables is the maximum acidity of the cheese examined, and it will be noticed that this point coincides with the time when the water-soluble phosphoric acid becomes 100 per cent of the total inorganic phosphoric acid in the cheese. An increase in the soluble calcium is noticed after this, but it does not seem to affect the acidity.

TABLE 1.—*Acidity determinations in Camembert cheese.*

Age of cheese.	Acidity of 100 grams of cheese.	Water-soluble phosphoric acid.	Water-soluble calcium oxid.
	cc tenth-normal alkali.	*Per cent total inorganic P_2O_5.*	*Per cent total CaO.*
2½ hours	24.0	73.53	39.02
10 hours	60.0	94.87	82.22
16 hours	100.0	100.00	97.62

TABLE 2.—*Acidity determinations in Cheddar cheese.*

Age of cheese.	Acidity of 100 grams of cheese.	Water-soluble phosphoric acid.	Water-soluble calcium oxid.
	cc tenth-normal alkali.	*Per cent total inorganic P_2O_5.*	*Per cent total CaO.*
When whey was drawn	48.0	50.98	27.93
6 hours	116.0	69.07	57.33
9½ hours	130.0	73.59	62.82
2 weeks	190.0	100.00	80.16

Mr. PATRICK. This paper suggests the question, Should we determine only the water-soluble acidity of cheese? O. Jensen has recently published an article in which he advises the determination of the acidity of the entire cheese, casein included. He recommends rubbing up the cheese with water and titrating the entire mass. There is certainly a difference of opinion as to which is the better method.

Mr. BOSWORTH. Such a determination would not be uniform, for the reason that the amount of free casein in two different cheeses might vary considerably, and the acidity of the water-soluble portion, depending upon conditions which are not under control in the manufacture of cheese, would not be determined.

Mr. Cochran. I noticed in the report on condensed milk that the sucrose determination is to be investigated. This subject has interested me of late, and I have been using acid mercuric nitrate to invert the sucrose in condensed milk with satisfactory results. This method, known as the Harrison method, was published in the Analyst about a year ago, but I have seen no reports of work done with it.

Mr. Patrick. I have found in using acid mercuric nitrate for sweetened condensed milk that there is danger of inversion taking place to some extent before the first polarization is made unless this is done immediately after filtration. A neutral solution of mercuric nitrate, proposed by Patein and Dufau, appears to be better than the acid solution.

REPORT ON FOODS AND FEEDING STUFFS.

By J. K. Haywood, *Referee.*

During the past ten years the attention of the referee on foods and feeding stuffs has been directed toward the collection and comparison of methods for determining moisture, ash, ether extract, crude fiber, albumenoids, starch, pentosans, and galactan. The official methods as they now stand represent the best of the above methods, from which the poorer methods have been gradually excluded. We all know that most of these methods give only approximate results, and that even these can not be obtained unless the most minute details of the method are followed to the letter. However, they are the best obtainable in the present state of our knowledge, and the details are as exact as a long series of comparative studies can make them. It seems, therefore, that a further comparison of these methods by different members of the association would be almost useless until decidedly new facts are ascertained regarding the separation and determination of cattle-food constituents.

When the last report was made on this subject, in 1903, the referee brought out certain facts in regard to crude fiber, which seem, however, to merit further study. Besides this, a method of determining a new constituent of cattle foods was recently published, i. e., methyl pentosans, which gives promise of being of some value. It is along these two lines, then, that the referee has worked. Samples for comparative study were not sent out, as it was thought best to devote all the time that the referee could spare to formulating the methods, so that they could be comparatively studied next year.

In 1903 a comparative study was made of the present official method of determining crude fiber; of the König method, by boiling with glycerol sulphuric acid for one hour, and of the modified König method, by boiling with glycerol sulphuric acid and then with 1.25 per cent sodium hydroxid. It was found that the present official method gave a fiber nearly free from albuminoids, but containing a large amount of pentosans; that the König method gave a fiber nearly free from pentosans, but containing considerable albuminoids, while the modified König method gave a fiber containing only negligible quantities of both pentosans and albuminoids. It was suggested by the referee, however, that the low results on fiber obtained by the modified König method were not only due to getting rid of all pentosans and albuminoids, but that a hydrolytic action on the cellulose of the crude fiber was exerted by the acid in the presence of glycerol, at a temperature of 131°–133° C. This suggestion was tested upon pure cotton cellulose, and when treated by the König method there was a loss of 12.35 per cent, due evidently to hydrolytic action. The referee was not willing

to condemn the König method on these figures alone and recommended a further study of the subject by the succeeding referee.

In working upon this subject as pure cellulose as possible was prepared by heating absorbent cotton, first with dilute sulphuric acid, then with dilute alkali, washing, and drying to constant weight. This cotton was used in all subsequent determinations. To ascertain just how much loss in weight there is by our present official method, a 1-gram portion of the cotton was boiled one-half hour with 1.25 per cent acid, under which treatment it lost 2.70 per cent in weight. Another 1-gram portion was then boiled one-half hour with 1.25 per cent sodium hydroxid, by which treatment it lost 17.06 per cent in weight. It is therefore evident that by our present official method there is a loss in pure cellulose of 19.76 per cent. With glycerol sulphuric acid and one hour's boiling there was a loss of 26.31 per cent, while with the modified König method there was a loss of 43.37 per cent. It is evident from the above that the modified König method is not an improvement on the old official method, since the great loss from hydrolysis of the cellulose makes an error in the minus direction greater than the plus error caused by the presence of pentosans in the crude fiber prepared according to the present official method.

It was hoped that a satisfactory method for determining crude fiber might be devised by using the König method and boiling only one-half hour instead of one hour with the glycerol sulphuric acid. This was done and it was found that the pure cellulose lost 29.40 per cent in weight. This loss in weight is almost 10 per cent greater than by the present official method. Such a showing would hardly entitle the method to consideration in comparison with the present official method, and it is therefore recommended that further work on the König method for determining crude fiber be abandoned.

The next subject studied by your referee was the determination of methyl pentosans in the presence of pentosans, by a method recently published by Ellett and Tollens.[a] This method is based on the following principles: First, it was shown by Ellett and Tollens that in certain vegetable materials both pentosans and methyl pentosans are present. On distillation with hydrochloric acid both of these distil over, the first as furfural, and the second as methyl-furfural. On precipitation with phloroglucol, the furfural-phloroglucid and the methyl-furfural-phloroglucid are precipitated. In the past both of these have been weighed together and calculated as so much phloroglucid, thus causing an error in the pentosan determination. Ellett and Tollens have worked out a method for the separation of these compounds, based on the solubility of the methyl-furfural-phloroglucid in alcohol, and the insolubility of the furfural-phloroglucid in the same medium. It is claimed by these authors that the solubility of furfural-phloroglucid in alcohol is practically negligible, so that the amount of material extracted from furfural-phloroglucid and methyl-furfural-phloroglucid represents the methyl-furfural-phloroglucid alone. It was with an idea of testing this method for determining methyl-pentosans and the underlying principles of the same that the following experiments were made.

It was first necessary to determine whether Ellett and Tollens were correct in saying that the furfural phloroglucid was practically insoluble in alchohol. For this purpose weighed quantities of arabanose (in quadruplicate), were distilled with hydrochloric acid, precipitated with phloroglucol, dried four hours, and weighed in a weighing bottle according to the official method. The weights of phloroglucid obtained, using two different weights of arabanose, in quadruplicate, were as follows:

0.0809, 0.0771, 0.0777, 0.0790 gram
and
0.2313, 0.2365, 0.2392, 0.2366 gram.

[a] J. Landw., 1905, *53* [1]: 13.

These were extracted with alcohol in the following manner: The weighed Gooch crucibles containing the dried phloroglucid were placed in a 100 cc beaker, and 30 cc of 95 per cent alcohol at 60° were poured into the Gooch. These beakers were then placed in a water bath and extracted for ten minutes at 60° C. All alcohol was sucked from the Gooch by a suction pump, poured back into the beaker, and passed through the filter again to catch particles of asbestos fiber. This alternate extraction and filtration was repeated three times. The last extract was only slightly colored.

The Gooch crucibles were finally dried in the water oven for two hours and again weighed in weighing bottles. The difference between the first and second weighings of the phloroglucid precipitates, representing the amount extracted by alcohol, were respectively as follows:

0.0039, 0.0028, 0.0033, 0.0032 gram

and

0.0033, 0.0045, 0.0034, 0.0040 gram.

This is an average of 0.0036 gram, a much greater amount than that which Ellett and Tollens found to be extracted, namely (0.0012 gram), so that it would appear that a correction of the methyl-furfural-phloroglucid obtained by subtracting this amount of material, i. e., 0.0036 gram, would be necessary, especially where the methyl-pentosans are very low, as they usually are with respect to the pentosans present.

Since it might occasionally be necessary to extract the phloroglucid precipitate more than three times to dissolve all of the methyl-furfural-phloroglucid, an experiment was next undertaken to ascertain what amount of furfural-phloroglucid is extracted by treating the precipitate five times with alcohol, as just described. For this purpose quadruplicate samples of arabanose were weighed out and determined as above; the amount of furfural-phloroglucid obtained was as follows:

0.0823, 0.0835, 0.0835, 0.0800 gram.

And the amount of the same extracted by five treatments with alcohol was:

0.0043, 0.0038, 0.0041, 0.0040 gram,

or an average of 0.0041 gram. It will thus be seen that the difference between the amounts obtained by three and five extractions is so small (0.0005 gram) that it is immaterial which number is made.

There is a very important point which is emphasized by this very slight difference in the amount extracted from the phloroglucid precipitate by three and five treatments. If the amount extracted from this phloroglucid precipitate by alcohol really represents the solubility of furfural-phloroglucid in alcohol, we would expect nearly twice as much to be extracted by five treatments as by three, but such is not the case. Further, on extraction with successive portions of alcohol the first extracts are much darker colored than the later ones, showing that more material is extracted in the beginning than subsequently. This again appears to indicate that the amount of material extracted does not really represent the solubility of the furfural-phloroglucid in alcohol. For these two reasons the writer is inclined to believe that either a very small amount of some secondary product extractable by alcohol is formed during the distillation of a pure pentose, in this case arabanose, or that some of the phloroglucol used for the precipitation is occluded by the precipitate, is not entirely washed out, and is finally extracted by the alcohol. For various reasons, difficult to explain, but evident to one who has used the method a few times, the referee inclines to the latter view. This is a matter which merits further study. However, whether this alcohol extract represents the solubility of furfural-phloroglucid in alcohol, is a secondary product, or is occluded phloroglucol, is not of special significance in separating methyl-furfural-phloroglucid from furfural-phloroglucid. The fact remains that a certain amount of some material is in the furfural-phloroglucid which is extracted by alcohol and is fairly constant in amount. This amount must be subtracted from the methyl-furfural-phloroglucid found before even fairly correct results are obtainable.

It was thought possible that on drying the phloroglucid for two hours extra, after extracting with alcohol, some oxidation of the precipitate would take place, so that

the difference in weight of the phloroglucid before and after extraction, according to the above method, would not give the true weight of the material extracted by the alcohol. To test this point, four samples of phloroglucid,[a] prepared by distilling arabanose as described above and precipitating it with phloroglucol, were treated just as the precipitates were treated in the previous case, except that alcohol was not placed on them, i. e., they were first dried for four hours, weighed in a weighing bottle, then removed from the drying oven and placed on filter pumps, where air was sucked through them for about the same period as when alcohol was used for the extraction. The phloroglucid precipitates were then returned to the water oven and dried for four hours instead of two, so that if any oxidation took place it would be apparent. The precipitates were finally removed from the oven and again weighed in weighing bottles. Working in this way one lost 0.0005 gram, two weighed exactly the same, and one lost 0.0010 gram. It is therefore evident that the phloroglucid precipitates do not oxidize and so gain in weight by the extra heating after the extraction with alcohol. It appears from this work that it would be safer to continue the second drying for four instead of two hours, since in two or three cases where the samples were dried only an extra two hours after having been treated as above, they had gained about a milligram in weight, but on further heating they returned to the original weight, showing that it was not an oxidation process that caused the gain.

It might be easier to evaporate the alcoholic extracts and weigh them directly, rather than to get the weight of the material extracted with alcohol by difference. This was done in all the above cases, and the alcoholic extracts by difference gave the following weights: 0.0039, 0.0028, 0.0033, 0.0032, 0.0033, 0.0045, 0.0034, 0.0040, 0.0043, 0.0038, 0.0041, 0.0040. By direct weighing, the following results were obtained: 0.0075, 0.0054, 0.0055, 0.0052, 0.0082, 0.0084, 0.0085, 0.0087, 0.0087, 0.0075, 0.0076, 0.0073.

From these determinations it appears that the average weight of the extract obtained from furfural-phloroglucid by indirect weighing was 0.0037 gram, while the average weight obtained by direct weighing was 0.0074 gram, just twice as much. This result was entirely unexpected, and up to the present time the writer is unable to explain it. At first it was thought that the 0.0074 gram was the true weight of the material extracted from the furfural-phloroglucid, and that the weight 0.0037 was lower than it really should be because of the oxidation of the phloroglucid in drying during the extra two hours. This supposition, however, was proved to be wrong by the experiment quoted above, showing that the phloroglucid does not gain in weight on further drying. It now seems that the only possible explanation of this amount of material in the residue from the alcohol extraction is that some reaction takes place between the material extracted and the hot alcohol, resulting in a heavier compound. This is also a question which must be studied before the method can be considered as well established.

Since Ellett and Tollens have made so many determinations showing that the methyl-furfural-phloroglucid is soluble in alcohol, it was not deemed necessary to test this point. In view of all the facts as stated the referee would recommend that the following slightly modified method of Ellett and Tollens be tested next year by the association:

Method for Determining Pentosans and Methyl Pentosans.

Proceed as in the determination of pentosans by the official method until the phloroglucid precipitate has been dried for four hours and weighed. Place the Gooch crucible containing this precipitate in a 100 cc beaker and pour into the Gooch 30 cc of 95 per cent alcohol heated to 60°. Place the beaker for ten minutes in a water bath

[a] It should here be mentioned that the phloroglucol used was an imported article, said to be free from diresorcol. It was further purified by the official method of the Association of Official Agricultural Chemists, Bureau of Chemistry Circular 30, p. 5.

heated to 60°. Remove the beaker and Gooch and suck from the Gooch all alcohol remaining therein with a suction pump. Repeat this alternate extraction and sucking dry of the precipitate three to five times, according to the color of the filtrate obtained. After the final extraction place the Gooch crucible in a wateroven and dry four hours, making the final weighing in a closely stoppered glass weighing bottle as described in the official method for pentosans.

The difference in weight between the furfural-phloroglucid plus methyl-furfural phloroglucid first obtained and the furfural-phloroglucid remaining after extraction with alcohol, minus 0.0037, represents the amount of methyl-furfural phloroglucid present, from which the original pentose (calculated as rhamnose) can be calculated by the following formula:

$$\text{Rhamnose}=(\text{Ph})\ (165)-(\text{Ph})^2\ (1.84)+0.010.$$

Ph equals the weight of methyl-furfural-phloroglucid; Rhamnosan equals rhamnose multiplied by 0.8. A table will be found on page 19 of the article of Ellett and Tollens,[a] in which attention is directed to an error in the calculation of 0.028 and 0.029 gram of the methyl-furfural-phloroglucid to rhamnose.

To obtain the weight of pentosans, subtract the final weight of methyl-furfural-phoroglucid obtained above from the weight of the mixture of methyl-furfural-phloroglucid and furfural-phloroglucid and calculate accordingly to Kröber's tables, or according to the formulas given in the present official methods for pentosans.

Working in this way the following results were obtained in quadruplicate on samples of gum arabic and tragacanth:

Quadruplicate determinations of pentosans and methyl pentosans made by the proposed method.

Determinations.	Gum arabic.	Traga-canth.	Determinations.	Gum arabic.	Traga-canth.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
Pentosans	26.18	37.03	Methyl-pentosans (as rhamnosan)	3.28	4.38
	25.60	36.94		3.54	4.54
	25.88	38.00		3.54	4.54
	25.36	36.92		3.58	3.98

REPORT ON SUGAR.

By C. A. Browne, jr., *Referee*, and J. E. Halligan, *Associate Referee*.

The work of the referee and associate referee upon sugar during the past year has been substantially along the lines recommended by the association at its last meeting and has comprised (1) work upon the more special methods of analysis in their relationship to sugar chemistry; (2) work upon purely chemical methods; and (3) work by a number of collaborators upon methods for the analysis of cane molasses, massecuites, and sugars.

In the investigation of special methods the work has been confined very largely to a study of the organic constituents of cane molasses. Methods for the estimation of nitrogen in the numerous forms under which it occurs in molasses have been compared, also methods for the determination of the nonfermentible sugars—a matter of considerable importance to distillers. The application of a method for analyzing sugar mixtures, read at the last meeting, has been extended to a wide range of sugars and carbohydrate bodies with a fair degree of success.

The work upon chemical methods has been continued by Mr. Munson, with the cooperation of Mr. Walker, the result being that we have a table for the estimation of

[a] Loco cit.

dextrose and invert sugar, both alone and in the presence of sucrose, under perfectly uniform conditions of analysis. Mr. Walker has lately added to this table columns for the estimation of lactose and maltose, and it is hoped that the work may be extended to other commonly occurring reducing sugars.

The present report will be limited entirely to a discussion of the cooperative work by various chemists upon a low grade massecuite, molasses, and sugar, the work of the referee on special analytical methods and of the associate referee on molasses methods having been combined. The three samples sent out for analysis were obtained from the Louisiana Sugar Experiment Station of New Orleans and represented the final products from sugar cane grown at this station the previous year. In the circular letter sent out with these samples the following instructions were given:

(1) WATER AND TOTAL SOLIDS.

Test as many of the following methods as possible:

(*a*) The official methods, page 27, Bulletin No. 46, Bureau of Chemistry.

(*b*) Drying 2 grams ten hours at temperature of boiling water, the loss at the end of this time being taken as water, without regard to constancy in weight.

(*c*) Drying in vacuum at 70° constant weight. The massecuite and molasses should be dissolved in an equal weight of water and about 2 grams of the solution weighed out upon sand or asbestos.

(2) REDUCING SUGARS.

(*a*) Determine reducing sugars as dextrose according to the method of Allihn, Bulletin 46, page 35.

(1) Upon the filtered solutions without clarification.

(2) Upon the filtered solutions after clarifying with 1 to 2 cc of lead subacetate.

(3) Upon the filtered solution after clarifying with an excess of lead subacetate, this excess to be removed by sodium carbonate (official method, Bul. 46, p. 33), or by potassium oxalate (Sawyer, recommendation 4, Cir. 26, p. 5).

(*b*) If desired compare the method of Allihn with that of Soxhlet or any other method preferred by the cooperator.

(3) SUCROSE.

Determine sucrose by the following methods:

(*a*) The official method by inversion (Clerget, p. 39, Bul. 46). The normal weight is made to 100 cc without dilution.

(*b*) By dilution (using Clerget's method as before).

(1) According to Sawyer, Circular 26, Bureau of Chemistry, page 5. Note carefully recommendations 1, 2, 3, and 5.

(2) According to Geerligs. A portion of well-mixed sample is dissolved in 1 to 4 parts by weight of water without heating. A normal weight of this solution is clarified, made up to 100 cc, and polarized in the usual way. If the solution is too dark to read in the 200 mm tube, read in the 100 mm tube.

(*c*) Compare the optical methods for sucrose with the official gravimetric method, Bulletin 46, page 39.

In reporting the results the cooperators are requested to report all analytical data as fully as possible—the methods used, dilutions employed, temperatures of polarization, manner of determining reduced copper, etc., in order to afford every facility for comparing the results.

It is also urged that the work upon the samples be begun, if possible, immediately upon their receipt to avoid the liability of changes in composition through fermentation.

C. A. BROWNE, Jr.,
Referee on Sugar (Special Analytical Methods).
J. E. HALLIGAN,
Associate Referee on Sugar (Molasses Methods).

Ten chemists signified their willingness to cooperate, and reports in whole or in part were received from five.

DETERMINATION OF TOTAL SOLIDS.

The results obtained by four of the chemists upon total solids are given in Table 1.

TABLE 1.—*Determinations of total solids in massecuite, sugar, and molasses.*

Method.	Time of drying.	H. P. Agee, sugar experiment station, New Orleans, La.			J. A. Hall, jr., sugar experiment station, New Orleans, La.			J. E. Halligan, agricultural experiment station, Baton Rouge, La.			S. F. Sherwood, Bureau of Chemistry, Washington, D. C.		
		Massecuite.	Sugar.	Molasses.	Massecuite.	Sugar.	Molasses.	Massecuite.	Sugar.	Molasses.	Massecuite.	Sugar.	Molasses.
	Hs.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
2 grams, 98°	10	82.09	95.65	78.66	82.12	95.87	79.16	82.20	95.42	77.66	82.21	95.40	77.93
2 grams on sand, 98°	10	82.40	95.63	78.50	81.40	.....	77.27	.....	.....	78.76	81.59	.....	77.86
	12	81.80	95.28	77.69	81.30	.....	76.86	.....	.....	78.04	81.30	.....	77.41
	16	80.98	95.09	76.66	Increase after 12 hours.			.....	.....	77.56	80.54	.....	76.66
	20	80.58	94.85	76.06	.....	.....	.....	.....	.....	.....	79.88	.....	75.89
	25	80.20	.....	75.65	.....	.....	.....	.....	.....	.....	79.66	.....	75.68
	30	80.10	.....	.....	.....	.....	.....	.....	.....	76.10	79.30	.....	75.20
2 grams with water on pumice stone, 98°	10	.....	.....	.....	82.22	.....	78.82	84.20	.....	80.02	81.85	.....	78.68
	12	.....	.....	.....	81.86	.....	77.88	83.54	.....	78.74	81.37	.....	78.02
	16	.....	.....	.....	81.43	.....	77.47	82.80	.....	78.18	80.70	.....	77.06
	30	.....	.....	.....	.....	.....	.....	81.08	.....	75.54	79.54	.....	75.89
	Ds.	45°	45°	45°			65°				25°	25°	25°
Hempel desiccator in vacuo, 2 grams dissolved on paper or asbestos	3	85.73	98.76	81.06	.....	.....	79.51	.....	.....	.....	85.08	96.98	81.98
	5	85.56	98.65	80.96	.....	.....	79.28	.....	.....	.....	84.88	96.79	81.34
	8	.....	.....	.....	.....	.....	.....	.....	.....	.....	84.59	96.77	81.32
	13	.....	.....	.....	.....	.....	.....	.....	.....	.....	84.27	96.69	81.04
								40°		40°			
	20	.....	.....	.....	.....	.....	.....	82.82	.....	79.26	.....	.....	.....
	40	.....	.....	.....	.....	.....	.....	82.26	.....	78.38	.....	.....	.....
Samples taken from Hempel desiccator and dried 8 hours in vacuo, 68°–70°											82.74	95.98	79.20

Mr. E. B. Holland, of the Massachusetts agricultural experiment station, obtained by a method of drying on quartz sand for twenty hours at 75° and then three hours at 100°, 82 per cent of solids in the massecuite, 95.27 per cent in the sugar, and 77.50 per cent in the molasses, these results comparing well with the 2-gram ten-hour method.

Some very interesting sets of experiments were submitted by Mr. B. L. Hartwell, of the Rhode Island experiment station, showing the effects of drying in a vacuum oven under varying conditions of temperature and pressure. During the drying, air which had passed through concentrated sulphuric acid a number of times was drawn through the apparatus. In one set of these experiments the drying was conducted for successive periods with phosphorus pentoxid placed in a dish inside the bath. The results of the experiment are given in Table 2.

TABLE 2.—*Determination of solids in massecuite and molasses by drying for consecutive periods under low pressure over phosphorus pentoxid with an air current drawn thorugh five sulphuric acid wash bottles.*

[B. L. Hartwell and P. H. Wessels, Agricultural Experiment Station, Kingston, R. I.]

Period.	Temperature.	Pressure.	Time.	Massecuite.		Molasses.	
				I.	II.	I.	II.
		mm.	*Hours.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	63°	16	17	82.95	82.86	79.06	79.28
2	58°	82	18	82.53	82.52	78.64	78.94
3	62°	95	20	82.27	82.19	78.43	78.70
4	70°	85	16	82.03	81.99	78.23	78.45
5	88°	48	16	80.97	80.89	77.17	77.42

In commenting upon these results Mr. Hartwell says: "The effect of drying at 88° illustrates how readily decomposition takes place when the temperature exceeds 70° and it is perhaps a question whether the gradual loss which has taken place by the continued drying is not due to some extent to decomposition rather than to moisture."

The results obtained by Mr. Hartwell after drying fifty-five hours at 62° show very close agreement with those obtained by Mr. Halligan after forty days drying in the Hempel desiccator. These results also correspond closely with those obtained by the different chemists by drying 2 grams for ten hours at 98°. The purpose of the work this year was to ascertain the most satisfactory method for determining moisture and solids in sugar products under ordinary laboratory conditions, and nearly all the cooperating chemists seem agreed that the 2-gram ten-hour method fulfils the conditions most perfectly. The results obtained this year, as well as during previous years, by this conventional method and the more accurate process of drying under diminished pressure at 60°–70° show a fairly close agreement. The method seems well adapted for routine laboratory work, and it is recommended that it be adopted provisionally by the association. Where vacuum ovens are available and greater scientific accuracy is desired, the method of drying upon some absorbent material at a lower temperature under diminished pressure is of course to be preferred.

The methods of drying on sand and pumice stone at the temperature of boiling water gave continual losses in weight on prolonged drying, though one chemist reported an increase in weight after twelve hours heating. Drying solutions of the materials upon paper or asbestos in a Hempel desiccator at the ordinary laboratory temperature will remove practically all of the moisture after standing many weeks. The process, however, is slow and not adapted for general work. Drying in a Hempel at 60° to 70° hastens matters considerably, the removal of moisture after one day at this temperature exceeding that obtained on thirteen days standing in the cold.

A difficulty is occasionally experienced by chemists in drying sugar-containing materials which are acid, owing to the rapid inversion and decomposition which set in. Pellet[a] advises the addition of a drop or two of ammonia in all cases before drying, to neutralize any such acidity, and this precaution seems to be worthy of attention.

Determination of Reducing Sugars.

The results upon reducing sugars as determined gravimetrically by Allihn's, and volumetrically by Soxhlet's, method are given in Table 3. For ease of comparison all determinations are reported in terms of dextrose, though the expression of results as invert sugar would be more accurate.

Table 3.—*Determinations of reducing sugars in massecuite, sugar, and molasses.*

Analyst.	Reducing sugars as dextrose, Allihn's method.*									Reducing sugars as dextrose, the Soxhlet volumetric method.		
	No clarification, solution filtered.			Clarified with 1–2 cc of lead subacetate.			Clarified with an excess of lead subacetate.					
	Massecuite.	Sugar.	Molasses.	Massecuite.	Sugar.	Molasses.	Massecuite.	Sugar.	Molasses.	Massecuite.	Sugar.	Molasses.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
H. P. Agee, sugar experiment station, New Orleans, La	26.60	7.22	31.74	25.62	7.18	31.00	25.04	7.04	28.54	26.66	7.10	32.68
J. A. Hall, jr., sugar experiment station, New Orleans, La	27.24	7.22	31.42	26.28	6.57	30.98	23.00	6.92	27.90	27.40	6.94	33.11
J. E. Halligan, agricultural experiment station, Baton Rouge, La	26.91	7.74	32.50	26.84	7.49	32.18	24.69	7.13	29.61	26.75	6.79	32.20
S. F. Sherwood, Bureau of Chemistry, Washington, D. C	†23.70	7.14	31.54	b22.89	6.82	30.84	.....	.....	.....	.....	.....	.....

* Reduced copper calculated from weight of cuprous oxid by all chemists.
† Low results due to leakage of molasses from sample during shipment.

[a] International Sugar Journal, 1906, p. 509.

A comparison of results shows that with the increasing addition of lead subacetate for clarification, a very marked falling off in the copper reducing power takes place in all the products tested. This, of course, brings up again the old question: "Should solutions be clarified or not before determining reducing sugars; and if so, how should they be clarified?" The question also arises: "Do these copper-reducing bodies, precipitated by lead subacetate, not belong to the non-sugars, and should they not be removed?" Pellet in numerous articles has contended that these precipitated reducing bodies consist largely of levulose, and the referee is also inclined to the belief that considerable quantities of reducing sugars are precipitated by the lead subacetate, not simply from the changes in reducing power and polarization—since this might result from the removal of reducing, optically active bodies which are non-sugars—but also from the decreasing yield of alcohol which fermented molasses solutions give after having been clarified with subacetate. There is no doubt that we have here one of the principal sources of the discrepancies found in determinations of reducing sugars, and for the sake of simplifying conditions the discontinuance of the lead subacetate solution entirely in clarifying solutions for the determination of reducing sugars would seem in many ways desirable, using for the purpose of removing slime and suspended impurities some inactive agent such as alumina cream. The point is one which should be fully investigated by next year's referee since the questions involved are of the greatest importance in commercial work. In this connection it may be noted that the English and French sugar chemists have not been uniformly favorable to the lead-subacetate clarification in the determination of reducing sugars, while the German chemists have been usually in favor of this preliminary treatment.

One very serious disadvantage of not clarifying our sugar solutions will be the greater care necessitated in the determination of the reduced copper, owing to the greater liability of the precipitated cuprous oxid being contaminated with organic and mineral matter. This is a frequent source of error even after clarification, nearly every chemist having had the experience at times of the cuprous oxid coming down green or yellowish colored, and retaining gelatinous organic or mineral impurities which render filtration difficult. Even when the precipitate is of the proper color there is no certainty of its being free from contamination, especially in case of saccharine products of low purity. To illustrate this point more fully, there are given in Table 4 a few results taken from a large number of comparative analyses made by Mr. S. F. Sherwood and Mr. M. H. Wiley at the Bureau of Chemistry upon a variety of products.

TABLE 4.—*Comparison of methods for estimating reduced copper.*

Analyst.	Material.	Reduced copper.			Remarks.
		From weight of cuprous oxid.	From weight of cupric oxid.	Volumetric method (Low).	
		Gram.	*Gram.*	*Gram.*	
S. F. Sherwood, Bureau of Chemistry, Washington, D. C.	Molasses residuum.	0.3753	0.3594	0.3494	Precipitate difficult to filter.
	....do	.3905	.3634	.3470	Do.
	....do	.2517	.2348	.2242	Do.
	....do	.3287	.3130	.3034	Do.
	....do	.3291	.3134	.3029	Do.
	....do	.2768	.2698	.2688	
	....do	.2709	.2620	.2612	
M. H. Wiley, Bureau of Chemistry, Washington, D. C.	Pure dextrose	.4619	.....	.4617	
	....do	.2449	.....	.2444	
	....do	.1251	.....	.1257	
	Beer	.0755	.....	.0753	
	....do	.0746	.....	.0748	
	Molasses	.4628	.....	.4520	
	Corn juice	.3360	.....	.3134	Do.
	Malt extract	.3322	.....	.3048	Large amount of peptones in extract.
	....do	.3160	.....	.2933	Do.
	....do	.2093	.....	.1934	Do.

In the results obtained upon the molasses residuum the precipitated cuprous oxid, after weighing, was ignited in a muffle and weighed as cupric oxid according to the method of the French chemists; the cupric oxid was then dissolved in nitric acid and the copper estimated by the volumetric method of Low. The results show a contamination of the cuprous oxid with organic matter as shown by the differences in copper as calculated from the suboxid and oxid and with mineral matter as shown by the differences in copper as calculated from the oxid and by the volumetric method.

With solutions of pure sugar and such liquids as beer, where the organic matter consisted largely of carbohydrates, the calculation of copper from the weight of cuprous oxid gave accurate results. In the case of the malt extracts, which contained added peptones, the precipitated cuprous oxid seemed to act somewhat as the copper hydrate of Stutzer's reagent and to carry down a considerable amount of albuminoid matter from solution; in the case of the molasses the precipitated copper seemed to be in partial combination with certain nitrogenous bases such as xanthin. The investigation of a suitable clarifying agent which will remove such contaminating bodies without precipitating the sugars, and the study of a rapid accurate method for estimating reduced copper, such perhaps as the electrolytic method with rotating anode, are offered as recommendations for next year's work.

The volumetric method of Low, suggested by Mr. Munson as a provisional method in his report of last year, has been tested by a number of the chemists with uniformly favorable results. Mr. E. B. Holland writes: "The method as a whole after a thorough trial proved perfectly feasible, being fairly simple and of easy manipulation, requiring no expensive apparatus." At the Bureau of Chemistry it was found that when large amounts of copper were present the end reaction was occasionally indistinct, otherwise the results were very satisfactory. The adoption of the method by the association is recommended provisionally.

Another error in the determination of reducing sugars by the customary methods is that resulting from the inversion of sucrose. This is particularly true of raw sugars in which the inversion of sucrose is always a disturbing factor. This inversion is especially pronounced in the methods of copper reduction which require long heating as those of Defren and O'Sullivan. By the latter method one of the cooperating chemists obtained 8.67 per cent of reducing sugars on the raw sugar, a result far in excess of that obtained by the other chemists using Allihn's method. The results by the latter method are also manifestly too high. Mr. P. H. Walker by the method of Munson and Walker obtained 6.56 per cent of reducing sugar as invert upon the sugar sample in question. The referee obtained 6.69 per cent by his method when a correction factor is used, and Mr. Sherwood obtained 6.74 per cent by the process of Meissl and Hiller—results closely agreeing yet considerably lower than the figures obtained by Allihn's method. Mr. Halligan states, as a result of his experience, that the Soxhlet method gives uniformly lower results than the method of Allihn, and that he prefers the volumetric method on the whole both for speed and accuracy. In the volumetric method when the solution is run in rapidly until nearly the point of complete reduction, the error from inversion of sucrose is considerably though by no means completely lessened.

Determination of Sucrose by Optical Methods.

The results obtained by the different chemists for sucrose by the optical method are given in Table 5.

TABLE 5.—*Optical determination of sucrose in massecuite, sugar, and molasses.*

[All readings corrected to normal weight, 100 cc, 200 mm tube.]

OFFICIAL METHOD.[a]

Analyst.	Massecuite.			Sugar.			Molasses.		
	Polarization.		Sucrose.	Polarization.		Sucrose.	Polarization.		Sucrose.
	Direct.	Invert.		Direct.	Invert.		Direct.	Invert.	
H. P. Agee, sugar experiment station, New Orleans, La	Impossible to read			+81.11	30° −24.86	*Per ct.* 82.47	Impossible to read.		
J. A. Hall, jr., sugar experiment station, New Orleans, La	do			+80.80	31° −25.30	82.57	Do.		
J. E. Halligan, agricultural experiment station, Baton Rouge, La	do			+80.71	32° −24.86	82.48	Do.		

DILUTION METHOD,[b] SAWYER.

Analyst.	Massecuite.			Sugar.			Molasses.		
	Polarization.		Sucrose.	Polarization.		Sucrose.	Polarization.		Sucrose.
	Direct.	Invert.		Direct.	Invert.		Direct.	Invert.	
H. P. Agee, sugar experiment station, New Orleans, La	+36.00	29° −17.16	*Per ct.* 41.28	+81.14	29° −25.30	*Per ct.* 82.74	+22.60	22° −15.40	*Per ct.* 29.51
J. A. Hall, jr., sugar experiment station, New Orleans, La	+36.00	28° −17.60	41.23	+80.86	31° −25.08	82.44	+22.52	31° −14.52	28.82
J. E. Halligan, agricultural experiment station, Baton Rouge, La	+36.80	30° −17.16	41.83	+80.70	32° −24.75	82.39	+23.04	32° −15.71	30.27

DILUTION METHOD,[c] GEERLIGS.

Analyst.	Massecuite.			Sugar.			Molasses.		
	Polarization.		Sucrose.	Polarization.		Sucrose.	Polarization.		Sucrose.
	Direct.	Invert.		Direct.	Invert.		Direct.	Invert.	
H. P. Agee, sugar experiment station, New Orleans, La	+36.24	30° −17.60	*Per ct.* 41.89	+81.24	30° −25.30	*Per ct.* 82.83	+22.76	22° −15.58	*Per ct.* 29.77
J. A. Hall, jr., sugar experiment station, New Orleans, La	+35.40	28° −17.86	40.97	+81.00	32° −24.57	82.47	+22.80	31° −14.96	29.39
J. E. Halligan, agricultural experiment station, Baton Rouge, La	+36.70	32° −17.60	42.42	+80.88	32° −24.20	82.03	+23.00	30° −15.84	30.34
C. A. Browne, jr., Bureau of Chemistry, Washington, D. C	+39.28	26° −20.4	[d]46.02	+79.52	24° −28.12	82.38	+19.04	−20.24	30.29

[a] 26.048 grams to 100 cc.
[b] 26.048 grams to 200 cc.
[c] 100 grams substance + 300 grams water. Normal weight of solution to 100 cc.
[d] High result due to leakage of molasses from sample during shipment.

All of the chemists reported inability to secure polariscope readings upon the massecuite and molasses by the present official method, requiring the use of a normal weight of material to 100 cc owing to the very dark color of the solution. This method, so far as low-grade sugar-cane products are concerned, has always been a dead letter with chemists, and a change as to the manner of preparing solutions for polarization is most desirable. Sugar chemists for many years past in their analysis of dark-colored products have employed some method of dilution, either diluting from 50 to 100

grams of material with a known amount of water and making all analyses upon the resulting solution, as advocated by Prinsen-Geerligs, or diluting a normal weight of products to 200 cc, 400 cc, or 500 cc, as proposed by Mr. Sawyer in his previous reports as associate referee on molasses methods. When a large amount of material is available the former method is usually preferred, owing to the opportunity of securing greater uniformity of sample, a matter of no small importance in the analysis of nonhomogeneous materials such as massecuite. The results of the chemists who compared the two methods by dilution show no appreciable difference, and it is recommended that these methods be adopted provisionally by the association.

An important question in connection with the polarization of low-grade sugar products is the lead precipitate error and what correction, if any, should be made for it. This subject has aroused a great deal of discussion of late among sugar chemists in all parts of the world; but the various arguments pro and con are too well known to require reviewing.

The influence of the strongly basic lead subacetate solution in precipitating reducing sugars has already been referred to, and this would naturally have the effect of increasing the rotation in the direct polarization. With low-grade sugar-cane products the lead error from this source is unquestionably far greater than that due to volume of precipitate. This error, however, applies only to the single and not to the double polarizations. It will be noted in Table 5 that the single polarizations upon the sugar and molasses show a wide variation between the results obtained in Louisiana and in Washington. In his own work the referee employed but a small amount of lead solution, and his direct polarizations are over 1 per cent lower with the sugar and nearly 3 per cent lower with the molasses. With double polarizations, however, the results are brought into very close agreement with those obtained by the Louisiana chemists.

A double polarization of raw cane products, whether of molasses, massecuites, or sugars, is manifestly more accurate when it comes to the question of true sucrose content. Only in very exceptional cases, such as those noted by Geerligs [a] in the analysis of Java products, resulting from strongly alkaline clarifications, do the reducing sugars have an optical rotation of approximately zero, in which case alone would single and double polarization give identical results. As a result of many comparative analyses made upon low-grade sugars from Louisiana and Cuba, the referee found that double polarization always gave higher results, the differences ranging from 0.60 per cent in the case of a sugar polarizing 89.80° to 3.88 per cent with a sugar polarizing 72.40°. The optical power of the reducing sugars in these samples varied from —20.6° to —46.9°, the general average being —34.5°. The theoretical value for the optical power of a normal weight of invert sugar in acid solutions, according to Clerget's formula, is —32.3° at 20° C. In other words, 1 part of invert sugar would neutralize 0.323 parts of sucrose at this temperature. Wiechmann [b] suggests the multiplication of the percentage of reducing sugars by the factor 0.34 and the addition of this result to the single polarization (17.5° C.) to obtain the true percentage of sucrose in raw sugars. The individual variations in the optical power of the reducing sugars in different samples are so great, however, that the use of such a factor can not be recommended.

In certain kinds of commercial work it is impossible from lack of time to make the double polarization, and for purposes of control in sugar-houses a single polarization, with proper regard to its limitations, is often sufficiently accurate.

The referee has spent a part of his time during the past year in search of a method which would give the true direct polarization, and for this purpose has compared the ordinary lead subacetate solution, Horne's dry subacetate method, Pellet's method, using hypochlorite of lime or soda and normal, lead-acetate solution, and a method in which no lead at all was used, employing a little alumina cream and a new, powerful

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[a] International Sugar Journal, 1906, p. 88. [b] Sugar Analysis, p. 99.

bleaching agent, sodium hydrosulphite. The results of this investigation, as far as it has been carried, show that the highest polarizations are always secured by the use of the subacetate solution, this being due both to the precipitations of reducing sugars from solution as well as to the volume of the precipitate. The dry subacetate method gave uniformly lower polarizations than the wet subacetate method, yet with this method there seemed to be also in some molasses a partial precipitation of reducing sugars. Pellet's method also gave lower polarizations than the wet subacetate method. The lowest polarizations were uniformly obtained when no lead at all was used, the solutions being simply bleached without any precipitation of sugars or interference by the volume of the precipitate. The sodium hydrosulphite is entirely without action upon the sugars, and the compound will be found of great service in the polarization of dark-colored products.

Determination of Sucrose by Chemical Methods.

The determination of sucrose in the three samples which were sent out by chemical methods was reported upon by a number of the chemists, but the results were not comparable on account of the different methods and calculation tables used. The referee has found a very general disagreement among chemists as to the proper interpretation of the official method for this determination. The method (Bul. 46, p. 39) reads as follows: "Determine first any reducing sugar in the sample, then invert the sucrose and redetermine the reducing sugar. Deduct the percentage of reducing sugar obtained at first and the remainder will be the reducing sugar derived from the sucrose. This multiplied by 0.95 will give the percentage of sucrose." The disagreement among chemists comes from the interpretation of the expression "reducing sugars." A number of analysts determine the sugar before and after inversion as dextrose,[a] and multiply the difference by the factor 0.95. Such a course is manifestly incorrect, since the factor 0.95 applies only to invert sugar. Other chemists determine the sugar before inversion as dextrose, levulose, maltose, lactose, or any other reducing sugar as the case may be, and that after inversion as invert sugar, usually according to different methods. This course is even worse than the former, since the reducing sugars present with the sucrose have been determined before and after inversion by entirely different methods and tables. As the official methods stands there is only one course to follow, and that is to determine the sugars both before and after inversion as invert sugar by the same method and table. The difference between these two results multiplied by 0.95 will give the true percentage of sucrose. The objection is raised that it would be incorrect to estimate the sugar before inversion as invert sugar, when sometimes it does not occur as such, as for example in a condensed milk. This objection, however, has no force when dealing with the sucrose determination. The object is simply to establish a zero point, so to speak, upon the invert sugar scale, and it makes no difference what the reducing sugar is, provided it does not suffer hydrolysis or destruction in the process of inversion. After the sucrose has been thus estimated the reducing sugar obtained before inversion may be changed to levulose, lactose, maltose, or any other reducing sugar, either singly or severally, by means of suitable conversion factors, in accordance with the principles given in the report last year upon the analysis of sugar mixtures.[b] In the particular instance of sucrose and any single reducing sugar the table of Munson and Walker may be used to great advantage;[c] the weight of copper from the reducing sugar before inversion will give on the same line the zero point on the invert sugar scale as well as the corresponding amount of dextrose, lactose, or maltose. The important point is that in working upon the analysis of sugar mixtures by reduction methods a strictly uniform method of procedure must be followed throughout.

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[a] This error in procedure appears in Bulletin 46, page 24, section 8 (b), in the method for the determination of sucrose in cattle foods.

[b] J. Amer. Chem. Soc., 1906, *28:* 439.

[c] Ibid., 1906, *28:* 663; 1907, *29:* 541.

As a result of the work comprised in the foregoing report certain recommendations were offered which are given on page 154, together with the action taken thereon.

REPORT ON CHEMICAL METHODS OF SUGAR ANALYSIS.

By L. S. Munson, *Associate Referee.*

The work of the past year on chemical methods of sugar analysis has been a continuation of that conducted for several years to establish uniform methods for the determination of the various reducing sugars. It is proposed that the same method of manipulation shall be used on all reducing sugars. Working along this line, tables have been prepared by Mr. Walker and the referee for pure dextrose, pure invert sugar, and mixtures of invert sugar and sucrose, and by Mr. Walker for pure maltose and lactose. The preparation of the solutions, the method of manipulation, analytical data, and tables for dextrose, invert sugar, and mixtures of invert sugar and sucrose have been presented in the Journal of the American Chemical Society [a] in detail. The results obtained upon lactose and maltose by Mr. Walker, together with full details as to the work, may be found in the same journal under the title of The Unification of Reducing Sugar Methods.[b] The two tables found in these articles give the necessary data for determining all of the more common reducing sugars.

Mr. Davidson, chairman of the committee appointed to invite the Secretary and Assistant Secretary of Agriculture to address the association, reported that the Secretary was out of town, but that the Assistant Secretary would address the convention at 10 o'clock on Friday morning.

The meeting adjourned.

THURSDAY—AFTERNOON SESSION.

THE CHEMICAL DETERMINATION OF SULPHITES IN SUGAR PRODUCTS.

By W. D. Horne.

The official methods of analysis include one for determining sulphites (SO_2) in wine by distilling with phosphoric acid (H_3PO_4) in an atmosphere of carbon dioxid, catching the distillate in standard iodin and titrating with sodium thiosulphate. As this method is seriously faulty, it is desired to call attention to the weak points and to suggest certain improvements with a view to revision.

In such a residual mother liquor as a refinery molasses there are apt to be organic substances which will volatilize from a boiling acid solution and be capable of reducing iodin. Therefore, instead of the above indirect method it would be much better to add hydrochloric acid and barium chlorid to the iodin solution and thus precipitate the sulphuric acid formed by the oxidation of any sulphites (SO_2) that have come over.

Further, some suitable precaution should be taken against error due to the evolution of hydrogen sulphid by the phosphoric acid (H_3PO_4) from any sulphids in the solution. That sulphids do occur in appreciable quantities in residual sirups has not yet been definitely settled, but that they may occur is possible from the fact that boneblack

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[a] June, 1906, *28:* 663. [b] April, 1907, *29:* 541.

used in refining sugar contains a little calcium sulphate which is slightly reduced by the carbon of the boneblack during revivication in the kilns to calcium sulphid, and traces of this are at times given up to the sugar solutions flowing from the boneblack.

The most promising method of separating hydrogen sulphid from sulphur dioxid in the distillate is to pass the distillate through a Woulff bottle containing a 2 per cent neutral solution of cadmium chlorid, which causes the immediate precipitation of hydrogen sulphid as cadmium sulphid, while the sulphur dioxid is not precipitated but passes on to the iodin, where it is oxidized to sulphuric acid, to be afterwards precipitated as barium sulphate.

As some sulphur dioxid may remain in the cadmium chlorid solution, it is simply necessary to filter the contents of the Woulff bottle into the iodin solution, thus separating any cadmium sulphid and introducing the sulphurous acid into the iodin, where it will be oxidized to sulphuric acid. The cadmium chlorid solution is without effect on either the iodin or the barium chlorid.

By this method one can avoid reporting sulphids and organic reducing substances as sulphur dioxid. Sulphid and sulphite if existing simultaneously in even moderate quantities will be somewhat decomposed when heated in the presence of phosphoric acid (H_3PO_4) and sulphur will be precipitated. It may be that they can not be given off together in appreciable quantities, but at any rate a preliminary test should be made for sulphids before proceeding with any quantitative determination. This can be conveniently done by acidifying the diluted and warmed sirup with phosphoric or hydrochloric acid, hanging a strip of filter paper moistened with lead acetate in the test tube and bubbling carbon dioxid into the bottom of the tube. If sulphids are present they will yield hydrogen sulphid, which will soon color the lead paper. The above method is offered tentatively to the association with the hope that it, or some better method, may be adopted in lieu of the present unsatisfactory mode of analysis.

Mr. Wiley. The problem discussed by Mr. Horne is of special interest, both from a legal and a scientific point of view, at this time, inasmuch as under the food and drugs act the determination of sulphurous acid in foods in general must be made, and errors in the methods for making such determinations call for special study. For example, the addition of mineral substances to confections is forbidden absolutely, not in large or small quantities, and, as sulphur dioxid is a mineral substance, its determination in such products entering interstate commerce becomes of importance. The mere trace of a substance, which possibly is present naturally, ought not to be considered as satisfactory evidence that it has been added, and, as the presence of sulphids in food products may result from the sulphur naturally present, the analyst should be able to discriminate clearly between a natural product in a confection or other food and an added substance; hence the importance of distinguishing between a sulphite and a sulphid, as pointed out by Mr. Horne. The unrestricted use of sulphur dioxid in food products is, however, far more general than it should be. For example, in sulphuring wine casks, the wine may be racked four or five times the first year, and possibly fifteen or twenty times before it is completely ripened, and, if at each racking sulphur candles of any desired size are burned, the

total amount of sulphur deposited is excessive. Already steps are being taken to prevent such excesses by fixing the length of candle to be used. Dried fruit is also sulphured to improve its appearance and protect it from insects; also, if sulphur is used, the evaporation need not be carried so far, and thus more water may be retained in the finished product. For these three reasons the sulphuring is often excessive, and the product is sometimes resulphured before packing. Apart from the question whether sulphur should be used at all in foods there is no doubt but what such excessive use should be prohibited, and the methods for accurately determining the amounts present are therefore of increasing interest and Mr. Horne's paper deserving of special attention.

REPORT ON MEDICINAL PLANTS AND DRUGS.

By L. F. Kebler, *Referee.*

The passage of the food and drugs act, June 30, 1906, is undoubtedly the most important occurrence affecting the status of drug products in this country since the last annual meeting of the association. As the standards prescribed by the United States Pharmacopœia are by this enactment made the basis for determining the quality of many drugs, and as future State legislation will undoubtedly be modeled on the Federal law prescribing the United States Pharmacopœia as the authority, the character and reliability of these analytical methods assume increasing importance. As a matter of fact, the Federal law with slight modifications has already been placed on the statute books of Georgia and Louisiana and adopted as the health code of New York City. In anticipation of governmental enforcement of the legal standards considerable criticism of the methods has appeared, and their merits will undoubtedly be thoroughly tested in connection with the administration of the law.

In designating the United States Pharmacopœia and National Formulary, official at the time of investigation, as the standards by which the law is in part to be interpreted, Congress apparently left open a way by which these standards may be modified by action of the organizations which revise and publish them. As preliminary steps toward such a modification, by means of a supplementary revision of the Pharmacopœia, have already been taken, the legal status of any alterations may have to be adjudicated. In this interesting and unprecedented situation the study of drugs must receive increased attention. State officials charged with the enforcement of the laws governing the adulteration and misbranding of foods and drugs must turn their attention to drugs as well as foods. Cooperative study of assay methods, if participated in and supported by those most directly interested in an equitable and effective administration of the law as applied to drugs, will result in very valuable contributions.

There is an element of truth in the idea that the assaying of drugs is beset with inherent difficulties and peculiar sources of error, and that in its present stage of development its results represent approximations to the truth in the interpretation of which some latitude must be allowed. This idea is especially urged in anticipation of the enforcement of the new legal standards of quality and purity.

The development of a high degree of accuracy in drug assaying is to be sought through an application of the same scientific principles which have improved other branches of analysis. The first necessity is a recognition of the nature of the difficulties to be surmounted. The obscure causes of variation in results must be determined and eliminated. They should not be tolerated and retained in methods under

the euphemism "personal equation," or "personal error." A real personal factor is obviously involved in using any of the senses as the standard of judgment, as sight in determining the end reaction of a titration, but unless the details can be so arranged as to reduce such personal equations to small proportions the method should not be considered satisfactory in principle nor infallible in the administration of law.

If the large differences in the results by certain methods reported by collaborators this year were entirely due to the personal factor in the strict sense of the term, they would furnish evidence of serious defects in the methods. In so far as they originated in lack of uniformity in manipulation, the obvious remedy is to determine the influence of such details and to embody in the directions explicit requirements regarding every detail which is found to be a material factor. The discretion which the methods allow in greater or less degree to the individual analyst must be intelligently and systematically curtailed. Only by such a process of elimination can the adaptability of the methods be ascertained and the issue narrowed to features which may be radically wrong or insusceptible of control. This, which is one of the principal objects of cooperative work, will be most effectively promoted if collaborators report not merely quantitative results, but also criticisms and suggestions. If exact compliance with the methods seems impracticable, the modifications adopted, and the reasons therefor, should be fully detailed. Ambiguity or indefiniteness in the directions as well as improvements in the manipulation should be indicated.

During the past year work on the methods for determining morphine in opium was continued and methods for ascertaining all or part of the alkaloidal constituents of cinchona, ipecac, and nux vomica were added.

Samples of these drugs, delivered as being of U. S. P. quality, together with the best available methods, were supplied to a number of chemists who signified a willingness to participate in the work, and complete or partial results were reported by ten collaborators.

The following directions were sent out with instructions that all calculations and solutions be based on the data contained in the United States Pharmacopœia, Eighth Revision:

POWDERED OPIUM.

Method I—United States Pharmacopœia, Eighth Revision,[a] with Additions.

Run duplicates on opium as received.

1. Weigh the crude crystallized morphine on watch glasses, as directed by the Pharmacopœia, and report weights.

Mix and powder the morphine of the duplicates and test mixture as follows:

2. Determine the purity by the limewater method of the Pharmacopœia, using 1 gram of the mixed crude morphine.

Report per cent purity.

3. "Mallinckrodt reassay."—Place 1.2 grams mixed crude morphine in an 80 cc Erlenmeyer flask, add 0.5 gram freshly slacked lime and 20 cc water, cork, and shake occasionally for one-half hour. Filter into a similar tared flask with gentle suction (reenforcing the point of the filter with a platinum or hardened paper cone), wash the flask and residue with limewater until the total filtrate and washings amount to 35 grams. Add 3 cc alcohol, 20 cc ether, rotate, add 0.5 gram ammonium chlorid, cork and shake vigorously.

Let stand two hours, then filter, dry, and weigh the precipitated morphine according to the directions of the Pharmacopœia. Report the weights obtained.

Method II—United States Pharmacopœia, Eighth Revision, Modified by Lamar.

Run in duplicate. Proceed as directed by Pharmacopœia to precipitation of morphine. To the 20 grams of aqueous extract add 60 grams of alcohol, stopple flask, shake well for one minute and set aside for thirty minutes, during which time the precipitated material should have completely subsided. Decant the clear supernatant liquid into a tared 250 cc evaporating dish, transfer the precipitate to a 7 cm filter pre-

[a] Abbreviated title "U. S. P. VIII."

viously moistened with a mixture of alcohol (3 parts) and water (1 part). The last portions of the residue are transferred to the filter by using small portions of the above hydro-alcoholic solution. The filtrate is to be collected in the tared evaporating dish. Continue washing the residue and filter by dropping the alcoholic solution on the filter and the residue until the filtrate is no longer bitter. Add 35 cc of water to the contents of the evaporating dish and evaporate on water bath to 14 grams, then proceed as directed by the Pharmacopœia.

Procure the same data for the morphine thus obtained as outlined under Method I.

Method III—Combination method.

Run in duplicate.

Macerate 12 grams of opium with water and proceed as directed by the U. S. P. VIII to 20 grams of aqueous extract in tared flask, using, however, sufficient rinsings to bring the weight to 22 grams instead of 20. Add 12 grams alcohol, exactly 0.6 cc ammonia water (10 per cent), and sufficient water to bring the total weight to just 36 grams. Rotate to mix and filter at once, cover to prevent evaporation, collect just 30 grams in a suitable tared precipitating flask. Add 25 cc ether, rotate, then add 3 cc ammonia water (10 per cent), stopper, shake vigorously for ten minutes, then proceed according to the U. S. P. VIII.

Procure the same data for the morphine, as outlined under Method I.

CINCHONA.

Run duplicates by each method.

Method I—United States Pharmacopœia VIII.

Determine total alkaloids and ether-soluble alkaloids and report results.

Method II—Total alkaloid.

Place in a 200 cc flask 2.5 grams of the cinchona with 5 cc of hydrochloric acid (10 per cent) and 15 cc of water, and digest on the steam bath for ten minutes. When cool, add 50 grams ether, 25 grams chloroform, shake, add 5 cc of sodium hydroxid solution (15 per cent), and shake for ten minutes. Add 1.5 grams powdered tragacanth and shake again. Filter off 60 grams through a funnel containing a pledget of purified cotton into a clean tared flask.

Extract by shaking out with successive portions of 20, 10, and 10 cc hydrochloric acid (1 per cent), or until no more alkaloid is yielded, as evidenced by the test with Mayer's solution applied to a drop. To the united acid extracts, collected in a separatory funnel, add 15 cc chloroform, shake, make slightly alkaline with ammonia water, and shake vigorously. When the chloroform separates, draw it off through a double filter into a tared 100 cc Erlenmeyer flask and repeat the operation twice with 10 cc chloroform; evaporate or distil off the chloroform in the flask, add 3 cc ether, evaporate, and dry at 110° to constant weight. Report weights.

Method III—Total alkaloid.

Place in a 200 cc flask 5 grams cinchona bark, add a mixture of 75 cc of ether with 25 cc chloroform, stopper the flask, shake and allow to stand for a few minutes, then add 5 cc of ammonia water, shake and allow to stand three hours, shaking at intervals. Decant as much of the mixture as possible into a suitable small percolator, the neck of which is plugged with a pledget of cotton, and receive the percolate in a separatory funnel containing 20 cc half-normal sulphuric acid, or sufficient to make the liquid distinctly acid after shaking. Rinse the contents of the flask into the percolator and continue the extraction with additional portions of the ether-chloroform mixture until the percolate gives no alkaloidal reaction, when a few drops are evaporated, taken up with acid, and tested with Mayer's reagent.

The separator is to be shaken vigorously for about one minute, the layers allowed to separate and the aqueous portion filtered through a pledget of purified cotton into another separator and the operation repeated with 10 cc more half-normal acid and then with 10 cc of water. To the combined acid filtrates in the second separator add 20 cc of the ether-chloroform mixture and slight excess of ammonia water. Shake out with three successive portions of the mixture, or until no more alkaloid is extracted, and collect the ether-chloroform solutions in a separator. Rinse with a few cubic centimeters of water, discard the latter, and draw off the ether-chloroform layer into

a tared flask or beaker. Evaporate slowly and carefully, to avoid spattering, to dryness on the water bath, add 3 cc ether to the residue, again evaporate to dryness, and dry at 110° in an oven to constant weight. Report weights.

Test the degree of exhaustion of the marc. Boil in a flask for ten minutes with 50 cc normal hydrochloric acid, cool, transfer the mixture to a percolator, the neck of which is provided with a pledget of cotton, collect percolate in a separator, rinse the marc with three successive portions of 10 cc of water, collecting all in above separator. Render the acid solution alkaline with potassium hydroxid solution and shake out with three successive portions of 10 cc of chloroform. Wash the combined chloroform solutions with a few cubic centimeters of water, discard the latter, and evaporate the chloroform carefully to approximate dryness in a tared beaker on the water bath. Add 3 cc ether, evaporate, dry at 110°, and report weight.

IPECAC.

Run duplicates by each method.

Method I—United States Pharmacopœia VIII.

(*a*) Give results by titration.

(*b*) Rinse the titration residue with water and ether into a separator, add slight excess of ammonia water, and shake out with successive portions, 25+20+10+10 cc of ether; at each separation draw off the aqueous layer to a second separator and transfer the ethereal layer to a third separator. The combined ether solution is rinsed with a few cubic centimeters of water, the latter discarded, the ether drawn into a tared flask, evaporated at temperature not exceeding 60° C., and the residue dried to constant weight in a desiccator. Report weights.

Method II.

Place in a 200 cc flask 6 grams finely powdered ipecac, 120 grams ether, 5 grams ammonia water, cork, and shake often for one-half hour. Let settle and filter off through a cotton plug in the neck of a funnel 100 grams (corresponding to 5 grams of ipecac) into a tared flask. Evaporate or distill off the ether and dissolve the residue in 5 cc alcohol, add 20 cc ether, 10 cc water, 3 drops hematoxylin solution and titrate with tenth-normal sulphuric acid, shaking strongly after each addition until the violet color changes to red-brown. Then add 30 cc water and continue titration to a lemon-yellow color. Report number of cubic centimeters of tenth-normal acid required.

Method III.

Place 5 grams finely powdered ipecac in a flask with about 50 cc ether, add 5 cc ammonia water, and shake frequently for an hour. Then decant into a small percolator, the neck of which is provided with a cotton plug, and rinse the remaining powder into the percolator with small portions of ether. Continue the percolation with ether until no more alkaloids are extracted; collect the ethereal percolate in a separator. Extract the ethereal solution by shaking out successively with 20+10+10 cc of normal acid. Combine the acid solutions, make slightly alkaline with ammonia water, and shake out mixture successively with 20+10+10 cc of ether. Combine the ethereal solutions, rinse with a few cubic centimeters of water, discard the latter, evaporate the ether in a tared flask, dry to constant weight in a desiccator, and weigh. Report weights.

NUX VOMICA.

Run duplicates by each method.

Method I—United States Pharmacopœia VIII.

In evaporating the chloroform solutions of the total alkaloids use a tared flask, and when the chloroform is apparently expelled add 3 cc ether, evaporate, dry to constant weight at 105°, and weigh total alkaloid before dissolving in acid.

Report (*a*) total alkaloid by weight, (*b*) strychnine.

Method II.

Place in a 150 cc flask 6 grams powdered nux vomica, 40 grams chloroform, 80 grams ether, cork, and shake frequently for one-half hour. Add 5 cc of (10 per cent) ammonia water, cork, and shake frequently for two hours. Then decant 100 grams exactly (equivalent to 5 grams of drug) into a flask, distil it to a residue of 10 grams, add 30 cc ether, 5 cc alcohol, 5 drops hematoxylin solution and 10 cc water, and titrate with tenth-normal acid to production of a red-brown color. Add 30 cc water and titrate to a lemon-yellow color as the end reaction. Report the number of cubic centimeters of tenth-normal acid required.

Acidify the titration residue with sulphuric acid, rinse into a separator, and shake out three times successively with small quantities of chloroform, discarding the latter. Make alkaline with ammonia water and shake out successively with 20+10+10 cc chloroform, or until no more alkaloids are extracted. Combine the chloroform solutions, rinse with a few cubic centimeters of water, discard the latter, and evaporate the chloroform to approximate dryness in a tared flask on a water bath. Add 3 cc ether to the residue, evaporate to dryness, and dry residue to constant weight in a desiccator. Report as total alkaloids by weight.

Method III.

Place in a flask 10 grams of nux vomica powder, add 100 cc of a mixture of 75 cc ether, 25 cc chloroform, 8 cc alcohol, and 3 cc stronger ammonia water. Cork tightly and macerate with frequent shaking for twelve hours. Decant as much of the mixture as possible into a suitable small percolator, the neck of which is plugged with a pledget of cotton, and receive the percolate in a separator containing 25 cc normal sulphuric acid, or sufficient to make the liquid distinctly acid after shaking. Rinse the contents of the flask into the percolator with a mixture of ether and chloroform (3 to 1), pack the powder with a glass rod, and continue extraction with the same mixture until the percolate gives no alkaloidal reaction when a few drops are evaporated, taken up with acid and tested with Mayer's reagent. The separator is to be shaken vigorously for about one minute, the layers allowed to separate, the aqueous portion filtered through a pledget of purified cotton into another separator, and the operation repeated successively with 20+20 cc more of half-normal acid and then with 10 cc of water. Make the combined acid filtrates in the second separator alkaline with ammonia and shake out successively with 25+15+15 cc of chloroform. Rinse the combined chloroform solutions with a few cubic centimeters of water, discard the latter, and evaporate the chloroform approximately to dryness in a tared flask or beaker on the water bath, add 3 cc of ether, again evaporate, and dry the residue to constant weight at 105°. Report as total alkaloids by weight.

The results submitted by the various cooperating analysts are given in the accompanying tables. In order to provide a common basis of comparison for the variability in results, obtained by different methods from the several drugs, the ratio of the difference to the average is given in the form of a percentage variation in addition to the average, maximum, minimum, and difference. It is to be noted, however, that these summaries do not include certain widely variant results (indicated in the tables), which apparently are not fairly representative. The significance of anomalous results is recognized, but their interpretation involves special considerations. An experienced and observant analyst can often associate an abnormal result with some unusual phenomenon in the operation, which would naturally lead to a repetition of the analysis. On the other hand, abnormalities may become apparent only upon compiling and comparing a number of results, as in this work, in which case it may be difficult to assign any cause for them. Such abnormalities militate somewhat against a method, even though the results are in the main satisfactory.

TABLE 1.—*Cooperative work on determination of morphine in opium by various methods.*

Analyst.	Method I.							Method II.							Method III.						
	Morphine on watch glass.	Average.	Purity by lime-water.	Morphine by lime-water.	Reassay morphine on watch glass.	Purity by reassay.	Morphine by reassay.	Morphine on watch glass.	Average.	Purity by lime-water.	Morphine by lime-water.	Reassay morphine on watch glass.	Purity by reassay.	Morphine by reassay.	Morphine on watch glass.	Average.	Purity by lime-water.	Morphine by lime-water.	Reassay morphine on watch glass.	Purity by reassay.	Morphine by reassay.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*
Asher	12.820	12.80	79.8	10.22	.....	.....	.....	10.350	10.38	93.9	9.74	.....	.....	.....	11.300	11.20	87.4	9.79	.....	.....	.....
Do	12.790							10.400							11.100						
Dolme	12.860	12.80	83.7	10.72	0.9170	76.4	9.78	11.150	11.18	95.8	10.71	1.0080	84.0	9.39	11.150	11.20	90.5	10.14	1.0040	83.7	9.38
Do	12.750							11.210							11.260						
Do	13.250	13.15	82.7	10.88	.9105	75.9	9.93	11.460	11.44	95.3	10.90	1.0010	83.4	9.54	11.840	11.93	90.4	10.78	.9890	82.4	9.83
Do	13.050							11.410							12.020						
Lyons	13.150	13.15	83.4	10.96	.9430	78.6	10.33	11.130	11.15	98.4	10.97	1.1150	92.9	10.36	12.090	11.44	88.7	10.72	1.0500	87.5	10.01
Do	13.100							11.170							10.800		96.0	10.37			
Do	13.190																				
Mallinekrodt	12.330	12.33	86.5	10.67	.9710	80.9	9.97	10.820	10.68	98.0	10.47	[a] 1.0898	90.8	9.70	10.920	10.72	97.4	10.45	[b] 1.0887	90.7	9.73
Do	12.330							10.540							10.530						
Parker	[c] 12.370	12.57	87.3	10.98	.9618	80.2	10.08	[c] 11.025	11.00	98.1	10.79	1.1197	93.3	10.26	[c] 10.980	11.01	99.7	10.98	1.1392	94.9	10.45
Do	[c] 12.770							[c] 10.975							[c] 11.048						
Do	[c] 11.653	11.91	90.7	10.80	1.0197	85.0	10.12	.....	.....	.....	.....	.....	.....	.....	[c][d] 11.262	11.20	98.7	11.05	.....	.....	.....
Do	[c] 12.165														[c][d] 11.137						
Do	[c] 12.729	12.54	85.2	10.68	.9535	79.5	9.97	.....	.....	.....	.....	.....	.....	.....	[f] 11.639	11.52	91.0	10.48	1.0350	86.3	9.95
Do	[c] 12.345														[f] 11.411						
Schulz	[g] 12.060	12.08	93.0	11.23	1.0830	90.3	10.91	[h] 10.810	10.77	98.2	10.58	1.1040	94.3	10.16	.....	.....	.....	.....	.....	.....	.....
Do	[h] 12.100							[h] 10.730													
Scoville	12.270	12.50	89.1	11.14	.9580	79.8	9.98	10.370	10.38	99.5	10.33	[i] 1.1090	92.4	9.59	10.980	10.80	97.8	10.56	.....	.....	.....
Do	12.730							10.390							10.620						
Stevens	10.599	10.68	98.3	10.49	1.1108	92.6	9.88	11.080	11.13	95.1	10.58	1.0600	88.3	9.82	10.695	10.64	99.4	10.57	1.1220	93.5	9.94
Do	10.753							11.180							10.575						
Wetterstroem	[f] 11.670	11.71	90.0	10.54	.9525	79.4	9.30	[f] 10.525	10.60	94.0	9.97	.9960	83.0	8.80	[f] 10.722	10.43	98.0	10.23	1.1280	94.0	9.81
Do	[f] 11.748							[f] 10.680							[f] 10.145						
Do	[f] 11.660	11.56	92.0	10.64	.9600	80.0	9.25	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Do	[f] 11.460																				
Average.	12.322	12.29	87.8	10.77	.9784	81.6	9.96	10.87	10.87	96.6	10.50	1.0669	89.2	9.74	11.10	11.10	94.6	10.51	1.0695	89.1	9.89
Maximum	13.250	13.15	98.3	11.23	1.1108	92.6	10.91	11.46	11.44	99.5	10.97	1.1197	94.3	10.36	12.09	11.93	99.7	11.05	1.1392	94.9	10.45
Minimum	10.599	10.68	79.8	10.22	.9105	75.9	9.25	10.35	10.38	93.9	9.74	.9960	83.0	8.80	10.145	10.43	87.4	9.79	.9890	82.4	9.38
Difference	2.651	2.47	18.5	1.01	.2063	16.7	1.66	1.11	1.06	5.6	1.23	.1237	11.3	1.56	1.945	1.50	12.3	1.26	.1502	12.5	1.07
Percentage variation	21.5	20.1	21.1	9.4	20.5	20.5	16.7	10.2	9.75	5.8	11.7	11.6	12.7	16.0	17.5	13.5	13.0	12.0	14.0	14.0	10.8

[a] Reported yield, 0.999 gram from 1.100 crude morphine.
[b] Reported yield, 0.998 gram from 1.100 crude morphine.
[c] Stood in refrigerator over night, 17 hours.
[d] Used 2.5 cc instead of 3 cc ammonium hydroxid.
[e] Stood at about 85° for 6 hours.
[f] Stood at about 75° for 17 hours.
[g] Stood in refrigerator 4 hours, shaken one-half hour.
[h] Stood in refrigerator 5 hours, shaken one-half hour.
[i] Reported yield, 0.970 gram from 1.050 crude morphine.
[j] Stood 12 to 14 hours at 12° C.

In principle the three methods studied this year differ essentially only in the manner and order of separating impurities. The original precipitate in Method I is assumed to be impure, the portion thereof soluble in limewater being accepted as the equivalent of pure morphine. In Methods II and III preliminary purifications of the solutions are undertaken to make practicable the precipitation of pure morphine, thus obviating the necessity of further treatment. The additional tests directed in this work are intended to measure the accuracy of these respective plans. The average per cent of limewater-purified morphine by Method I (10.76) should be compared with the average per cents of morphine as precipitated by Methods II and III, which are 10.87 and 11.10, respectively. The limewater-correction results by Methods II and III are 10.50 per cent and 10.51 per cent, respectively.

From these data the original results by Method II are fairly in accord with the corrected results by Method I, and the preference between the two methods is therefore a question of expediency rather than of accuracy. The original results by Method III, however, vary through a somewhat wider range and the percentage of impurity associated with the morphine is materially higher. The inferiority of Method III in its present form is therefore apparent. A comparison of the crude and the purified morphine by Method I tends to confirm former observations, namely, that the impurity varies practically independently of the amount of morphine. Stevens's results confirm our former observation, namely, that it is possible to precipitate a very pure morphine and obtain an amount approximating closely the best results. Schulz's results are significant. It will be noted that he obtained considerably the highest corrected result, and next to Stevens the highest purity, by shaking thirty minutes and precipitating five and six hours. The influence of the time and manner of shaking and the temperature and period of precipitation upon the amount of original precipitation in Method I has often been pointed out, and it is not improbable that these factors affect the morphine as well as the impurities. A more detailed study of these points seems advisable.

Method III is an adaptation of the principle of purification by partial precipitation with ammonium hydroxid, introduced by Dieterich, and embodied in the method of the German Pharmacopœia, third edition. The aliquot feature is replaced by total extraction of the opium. The precipitation is made in presence of alcohol, as in Method I. The preliminary results obtained in the drug laboratory by this method were encouraging. Some collaborators, however, experienced difficulty in obtaining the 30 grams of filtrate after addition of ammonium hydroxid, and the slow filtration involved exposure to evaporation. The operation might probably be expedited by providing a larger amount of opium and solvents from which to filter 30 grams. But the objection seems well taken that the same amount of ammonium hydroxid would not be suitable for different opiums. On the whole the method does not seem adapted to produce as pure morphine as Lamar's (Method II).

As stated in the report of this work for 1905, the experience of two years shows that nothing is gained by removing the morphine from the counterpoised filters for weighing and the results are 0.1 to 0.2 per cent lower. Further study of this point seemed needless, and weighing on watch glasses was directed simply because it is the pharmacopœial method.

Limewater undoubtedly dissolves some of the impurities precipitated with the morphine, and the purity factor thus obtained is too high. Lyons believes that time is a factor in this solubility, and that a portion of the impurity first dissolved will reprecipitate on standing. The color alone is ocular evidence of soluble impurity in the limewater solution, and according to present theories the calcium ammonium meconate of the original precipitate is by limewater changed to calcium meconate, which may complicate matters.

Unsuccessful attempts have been made in the drug laboratory to determine volumetrically the morphine in the limewater filtrate. One method was to determine the total alkalinity of the solution in comparison with a blank experiment with the same limewater, the increased alkalinity being attributed to morphine in solution. The other method was based upon the alleged acid or phenolic reaction of morphine toward Poirrier's blue, according to which in parallel experiments the morphine should produce a decrease of alkalinity by neutralization of the lime. The experiments failed for lack of definiteness in the end reactions. The addition of alcohol proved of no advantage.

The Mallinckrodt reassay has been suggested as a useful check on the purity of morphine precipitates. It is not expeditious, and its results need correction by factors not yet well determined. The need of an accurate (even though tedious and complicated) assay process for opium as a standard of comparison for shorter technical methods is obvious, and in view of the recognized defects of the limewater correction it seems expedient to attempt to control results by an additional method.

From considerable experience with the reassay method, Mallinckrodt believes that a correction of 20 to 30 milligrams should be added to the weight of reassay morphine for solubility in the mother liquor, which would be equivalent to raising all results about 0.21 per cent. A few blank experiments with practically pure morphine in the drug laboratory indicated that the solubility at 25° to 28° is about 30 milligrams. On the other hand Mallinckrodt's experiments seem to show that the morphine obtained by this method is only 97 to 99 per cent pure. Three or four reprecipitations seem to be necessary to eliminate all the impurities. The application of a correction factor should be subject to future experiments.

Lyons questions the use of alcohol in the reassay, and also thinks less ether would be preferable. He has obtained encouraging results by the substitution of liquor calcis saccharatus (British Pharmacopœia) for lime, both in the reassay and in opium assays, but he especially recommends a trial of Flückiger's suggestion, the preliminary removal of calcium from the opium solution by means of ammonium oxalate. A pair of duplicates run by this method in the drug laboratory gave an average total of 11.85 per cent—corrected by limewater, 10.94, and by reassay, 10.26 per cent.

Lyons also objects to the pharmacopœial direction that the precipitate be washed with morphinated alcohol, as moderate changes in temperature affect the solubility, causing the solution to deposit or dissolve morphine, and also morphine is apt to be deposited by evaporation. He prefers liberal washing with morphinated water, and drying the filter between folds of absorbent paper.

Cinchona.

The sample of cinchona bark sent out was below the standard, which is not less than 5 per cent of total alkaloids and at least 4 per cent of ether-soluble alkaloids. This circumstance is favorable to the method, which might give low results with rich barks owing to imperfect extraction. The fineness of the powder also favors complete extraction. None of the methods can, on the whole, be regarded as entirely satisfactory in view of the results reported.

The results by Method I average 3.49 per cent, with a variation of 19.5 per cent. The figures do not suggest any single or predominant cause of variation. Comparing them with the results of Method III, which is the best one available, the average total, 3.49 per cent, by Method I, is in substantial agreement with the average total, 3.37 per cent, by Method III. In fact, if the latter result be corrected by excluding the results of two analysts the average totals for both methods are 3.49 per cent. This affords no support to the criticism that aliquot methods like Method I are likely to yield high results owing to the fact that the aliquot portion of the solvent contains more than the theoretical fraction of the active constituents of the drug. The possibility of a compensating loss elsewhere in the process must not be overlooked. In this connection it

may be noted that Method I assumes that 125 cc of ether plus 25 cc of chloroform makes 150 cc of ethereal mixture. Though the resulting condensation in volume may be insufficient to lead to materially higher results, it would be better in principle to measure 150 cc of a similar mixture after cooling.

Regarding possible causes of the differences in the results by Method I the following suggestions received seem especially worthy of note. Lyons considers the amount of acid directed to be used in shaking out the ethereal solvent insufficient to extract the latter thoroughly. This would make both the total alkaloid and the ether-soluble alkaloid low, other considerations being equal. Parker questions the suitability of the graduated cylinder for dividing the 50 cc of acid solution into equal parts. An error in the division would give a total alkaloid gain at the expense of the ether soluble or vice versa. Inspection of the results reveals examples apparently supporting both criticisms, but the extreme variations in the ether-soluble results are probably due in great degree to other causes.

Method II is Fromme's method.[a] The results by this method would, as a whole, appear to be extremely unfavorable, with the low average total of 3.10 per cent and the very high percentage variation of 60.9. Inspection shows that the results may be separated into two groups, one containing the 8 results of Dohme, La Wall, Parker, and Schulz with an average of 3.68, maximum 3.94, minimum 3.45, and percentage variation of 13; the other separated by the marked interval of 0.87 per cent, containing 6 results by the remaining three analysts with an average of 2.33, maximum 2.58, minimum 2.05, and percentage variation of about 23. Wetterstroem's result of 1.68 is excluded as anomalous.

It seems reasonable to conjecture that this peculiarity is due to some single difference in the manipulation which might be revealed if a careful comparison of notes were possible, and which might place the method on a better basis. One of the principal criticisms made by Asher and Lyons, who obtained low results by Method II, is that the maceration period (ten minutes) is too short. It would seem that the preliminary digestion with hydrochloric acid justifies some shortening of the time of maceration. Dohme attributes his higher results by Method II to the larger proportion of solvent to drug than was the case in Method I, causing a more complete extraction. Such a difference might be more apparent with a richer bark. Parker suggests that the variations might be less (though more time might be necessary) if the quantity of bark were doubled and the other quantities increased in proportion; also that the filtration of alkaloidal solutions, especially as applied in this case, through double filters, is an operation to be regarded with suspicion in view of the imperfectly known phenomena of adsorption and the doubt of thorough washing. Method III, as a simple total extraction method, was intended to furnish a check upon the preceding two. The results are in a measure disappointing, the percentage variation being 22. Analysis of the results show that they fall into groups, not so marked but similar to those discussed in connection with Method II. If the considerably lower results of Asher and Lyons be set aside, the average total of the remaining results is 3.49 per cent and the percentage variation only 11. That the variability is partly due to imperfect extraction is indicated by the fact that all the low results correspond to high yields of alkaloid from the marc. The amounts of alkaloids extracted from the marc show plainly that failure of the last portion of ethereal percolate to respond to the test for alkaloid with Mayer's reagent is no proof of exhaustion of the drug, and that additional treatment is advisable. Preliminary digestion with acid (analagous to Method II) with subsequent drying is suggested. Lyons points out that the alkaloid extracted from the marc in the manner directed is impure and that purification by re-solution in acid and shaking out again may materially reduce the amount.

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[a] Cæsar and Loretz, Geschäfts-Bericht, 1905, p. 44.

TABLE 2.—*Determination of alkaloids in cinchona, ipecac, and nux vomica.*

Analyst.	Cinchona.					Ipecac.				Nux vomica.				
	Method I.		Method II.	Method III.		Method I.		Method II.	Method III.	Method I.		Method II.		Method III.
	Alkaloid.			Alkaloid.		Alkaloid.		Alkaloid. by titration.	Alkaloid. by weight.			Alkaloid.		Alkaloid by weight.
	Total.	Ether soluble.	Total alkaloid.	Total.	From marc.	By titration.	By weight.			Total alkaloid.	Strychnine.	By titration.	By weight.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Asher	3.40	2.3	[a] 2.37	3.00	0.20	1.67	1.75	1.77	1.74	3.04	1.11	3.03	3.18	2.76
Do	3.60	2.16	[a] 2.38	3.02	.22	1.67	1.74	1.75	1.72	3.01	1.10	2.98	3.14	2.73
Dohme	3.52	3.0	3.65	3.52	.16	1.86	1.73	1.88	1.92	.....	1.39	2.82	3.00	[b] 3.06
Do	3.44	3.14	3.75	3.46	.14	1.85	1.76	1.83	1.91	3.29	[c] 1.42	2.75	3.02	[b] 3.15
La Wall	3.50	3.08	3.60	3.40	.08	[a] 1.23	[a] 1.35	1.57	.....	.....	.....	.....	.....	.....
Do	3.52	3.02	3.45	3.36	.10	[a] 1.42	[a] 1.50	1.67	.....	.....	.....	.....	.....	.....
Lyons	3.38	[d] 2.50	[a] 2.58	3.04	[e] .27	[f] 1.70	1.92	.....	[g] 1.92	2.70	[h] 1.20	2.73	3.00	2.93
Do	3.25	2.79	[a] 2.54	3.15	[f] .18	[f] 1.73	1.85	.....	[g] 1.88	2.91	[j] 1.16	2.75	3.00	2.97
Do	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.72	(*k*)	.....	.....	.....
Parker	3.40	[l] 3.12	3.58	3.55	.116	[m] 1.68	1.76	1.62	2.04	3.20	[na] 2.35	2.74	2.98	3.07
Do	3.41	[l] 3.11	3 59	3.54	.204	[m] 1.66	1.76	1.62	2.11	3.21	[na] 2.43	2.74	2.92	3.02
Do	.....	[o] 2.63	.....	.....	.....	[p] 1.60	1.72	.....	.....	[q] 3.02	[r] 1.35	2.68	2.90	3.05
Do	.....	[o] 2.66	.....	.....	.....	[p] 1.74	1.73	.....	.....	[q] 3.04	[r] 1.26	.....	.....	3.00
Do	.....	[s] 2.65	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Schulz	3.93	2.80	3.94	3.74	.....	[t] 1.92	.....	1.86	1.88	3.16	1.33	2.67	3.00	2.89
Do	3.80	2.20	3.85	3.58	.....	[p] 1.63	.....	1.90	1.84	3.04	1.33	2.75	3.06	2.88
Do	3.30	2.28	.....	.....	.....	[t] 1.87	.....	.....	.....	.....	.....	.....	.....	.....
Do	3.58	2.38	.....	.....	.....	[t] 1.99	.....	.....	.....	.....	.....	.....	.....	.....
Wetterstroem	3.55	2.84	[a] 1.68	3.40	.....	[p] 1.62	1.98	[p] 1.97	1.68	.....	[p] 1.06	3.00	3.14	3.11
Do	3.32	2.83	[a] 2.05	3.38	.....	[p] 1.68	1.93	[p] 1.90	1.66	.....	[p] 1.05	3.00	3.18	3.13
Do	3.39	2.98	[a] 2.05	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Do	3.48	2.70	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Average	3.49	2.72	3.68	3.37	.167	1.74	1.81	1.78	1.86	3.03	1.23	2.81	3.04	2.98
Maximum	3.93	3.14	3.94	3.74	.27	1.99	1.98	1.97	2.11	3.29	1.42	3.03	3.18	3.15
Minimum	3.25	2.16	3.45	3.00	.08	1.62	1.72	1.57	1.66	2.70	1.05	2.67	2.90	2.73
Difference	.68	.98	.49	.74	.19	.37	.26	.40	.45	.59	.37	.36	.28	.42
Percentage variation	19.5	36.03	13.30	22.00	114.00	21.30	14.4	22.50	24.20	19.50	30.10	12.50	9.20	14.00

[a] Not included in maximum, minimum, or average.
[b] Dried at 60°.
[c] By weight.
[d] Temperature during shaking reduced below 15° C., and shaking continued ten minutes.
[e] Dissolved in acid water, filtered, and reextracted with ether-chloroform =0.124 per cent.

f Original weights of alkaloid 2.19 and 2.10 per cent, respectively.
g Results of titration 1.78 and 1.74 per cent, respectively.
h Strychnine, by weight, 1.22 per cent.
i Determined by mixing the drugs with slaked lime, moistening with water, drying, and extracting with hot alcohol. This crude alkaloid was purified by solution in acid, washing with ether and shaking out.
j Strychnine, by weight, 1.23 per cent.
k Strychnine, by British Pharmacopœia assay, 1.23 per cent; by weight. 1.26.
l Cooled to 14° in refrigerator before adding ammonia water. This addition and removal to shake permitted temperature to rise above 15°, but probably not above 20°.
m Used hematoxylin.
n Nitric acid did not react well. Not included in maximum, minimum, or average.
o After cooling to 10° added the ammonia water, then cooled to 6° before shaking, during which time the temperature rose to 16°. Kept it between 14° and 16° by means of a water bath.
p Used cochineal.
q Dried at 115° C.
r Nitric acid reacted well.
s Used a bath kept at 15°, but it was impracticable to shake without removal from bath and rise of temperature. The temperature was 15° when separated at end of ten minutes.
t Used more indicator than United States Pharmacopœia directs.

The results on ether-soluble alkaloids by Method I vary over a range of 36 per cent, which is unsatisfactory. The average is 2.72, maximum 3.14, and minimum 2.16 per cent. Parker's results alone indicate the cause of the differences. Criticisms received and observations made in the drug laboratory point strongly toward indefiniteness regarding temperature conditions and practical difficulties in carrying them out. Lyons considers that it has been demonstrated that practically all the cinchonine is separated by ten minutes continuous shaking at a temperature as low as 15°, and obtained his results in that manner. By following the pharmacopœial directions, agitation will take place at a temperature below 20°, but not necessarily as low as 15°. Two minutes shaking within this range of temperature often hardly starts crystallization, which proceeds rapidly at a somewhat lower temperature. Though too few in number to justify a definite conclusion, the results of Parker tend to support the view that two minutes shaking is sufficient under proper temperature conditions, but that the latter should be rigorously prescribed. To maintain a uniform temperature in warm weather, during the shaking and standing period, is not an easy matter without some special arrangements, and the improvising of these is left entirely to the analyst. Unless the solution is chilled below 15° to begin with, the addition of the ammonia water and the shaking are likely to raise the temperature above 20°. If a constant temperature bath be used and the separator removed and shaken, the temperature of the contents will rise in warm weather, and some arrangement for shaking in the bath seems necessary. The ether used for rinsing should also have the same temperature as the main portion. It is sometimes difficult to separate the ether solution clear, the crystals remaining in suspension. After tapping off the aqueous layer the ether solution can be better decanted through the mouth of the separator, thus avoiding contamination with portions of the aqueous layer adhering to the inside of the lower outlet. The neck of the separator should finally be washed with ether.

In connection with both the total and ether-soluble determinations of Method I, the comment is made that for gravimetric determinations, unless good reasons to the contrary exist, the final ether-chloroform solutions (obtained by shaking the alkaloid out of aqueous solutions) containing soluble salts (in this case ammonium sulphate) should be rinsed with a small amount of water before evaporating. Otherwise the ether may carry enough saline matter in solution to give high results. The mutual solubilities of water, ether, and chloroform should not be ignored.

Ipecac.

If all results were included, pharmacopœial Method I would appear at a disadvantage with a 45 percentage variation. By eliminating the low results of one worker the percentage variation is reduced to 21.3, which compares favorably with those of Methods II, 22.5, and III, 24.2. Even by excluding these results it is apparent that Methods I and II give lower results than Method III. Aliquot Methods like I and II have been charged with a tendency to yield high results due to several inherent errors. If such be the tendency it does not appear in these figures. Possibly the maceration period of one-half hour is too short. The gravimetric modification of Method I evidently gives more uniform results than the pharmacopœial titration method.

In Method I the questionable principle is adopted of assuming that 115 cc of ether and 35 cc of chloroform are equivalent to 150 cc of the mixture. The necessity of the admixture of chloroform is not apparent and the use of ether alone, with a smaller proportion of drug as in Method II, might repay trial. The agglomeration of the drug can not be produced by 10 cc of water, 18 to 20 cc being necessary. The shaking out of the alkaloid from the alkaline solution before titration as directed is at times incomplete.

Wetterstroem obtained no definite end reaction with hematoxylin in Method I and used cochineal in all titrations. The experience of the drug laboratory with hematoxylin in Method I was very unsatisfactory. When used in the amount directed

(5 drops), no definite end reaction could be obtained with either freshly prepared or old solutions of two different samples of the indicator, all of which in blank tests proved sensitive to the titrating solution, fiftieth-normal potassium hydroxid. The first apparent and best marked change was a fading away of the slightly yellowish tint of the alkaloidal solution. On adding fiftieth-normal potassium hydroxid drop by drop the solution very gradually assumed a smoky bluish-gray appearance, with apparent separation of alkaloid. No purple or violet color was obtained. With 30 drops of hematoxylin solution slightly better results were produced, the color with excess of alkali being a pale smoky blue. The results of various experiments, which it is impracticable to describe here, seemed to indicate that neither carbonic acid nor overheating of the alkaloid is the disturbing factor, but that the alkaloidal sulphate interferes with the color reaction between the free alkaloid and hematoxylin, and strengthened the impression that this indicator is not adapted to the titration of ipecac alkaloids as directed in Method I. Cochineal gave a much more satisfactory end reaction.

Method II is that of Panchaud. The titration to an acid reaction with hematoxylin (an inversion of the usual method) is characteristic of Panchaud's scheme of analysis, which will probably be adopted for a number of drugs in the forthcoming revision of the Swiss Pharmacopœia. It has the supposed merit of eliminating the usual back titration with alkali.

In the drug laboratory the end reaction with hematoxylin in Method II, while not entirely satisfactory, was considered less liable to cause large errors than the conditions of Method I. Considering the simplicity of Method III, the results show surprising variations. Possibly the directions do not insure thoroughness in the extraction and shaking out processes.

Nux Vomica.

By Method I the variation in total alkaloid was 19.5 per cent, or, excluding Lyons's low results, only 9 per cent; in the strychnine titration, excluding Parker's two high results, 30.1 per cent. In Method II the variations were, by titration 12.5 per cent, by weight 9.2 per cent, and in Method III, 14 per cent.

In Method I the pharmacopœial directions for measuring 200 cc of the prepared ethereal mixture commendably depart from the principle criticised under "Cinchona" (I) and "Ipecac" (I). Particles of the drug are likely to float in the ethereal liquid, and it would be advisable to decant the latter through a small percolator provided with a pledget of cotton in the neck. The shaking out with normal sulphuric acid as prescribed does not remove all the alkaloidal matter and should be repeated until Mayer's solution gives no reaction. Traces of alkaloid were still extracted after shaking out three times more with 5 cc of the acid.

Parker assayed the remaining ethereal solution and marc from the two total alkaloid determinations under Method I, which yielded 3.02 and 3.04 per cent. The marc was extracted successively with chloroform, hot dilute sulphuric acid, and alcohol, the combined solutions concentrated and shaken out. By this procedure these portions yielded 2.89 and 2.87 per cent, respectively, by weight. This would indicate that the sample contained 2.95 per cent of total alkaloids, which is in close agreement with the results by Method III and supports the theory that the aliquot methods give slightly high results.

The results of the strychnine determinations are quite irregular. Experiments in the drug laboratory readily located a source of error in the reaction between nitric acid and brucine. It was repeatedly observed (about one time in four) that under apparently identical and strictly pharmacopœial conditions, the characteristic red color developed sometimes promptly, sometimes slowly, and sometimes not at all, even after hours. In one case the alkaloid was recovered, again subjected to the nitrating process and recovered, and still gave a strong reaction for brucine.

Examination of the literature showed that the pharmacopœial method has also given erratic results in the hands of other analysts, and that the causative factors have not been fully determined.

Howard,[a] working with Keller's method, concluded that the temperature is an important factor, and obtained the best results by nitrating at 0°.

Farr and Wright[b] using the pharmacopœial process found that only 9 per cent of the brucine was destroyed at "ordinary temperatures," and not quite all at 38° in ten minutes or at 50° in five minutes, but that it was entirely destroyed at 50° in thirty minutes. In their formal directions, however, they direct the use of 3 cc of nitric acid sp. gr. 1.42 (instead of the U. S. P. sp. gr. 1.40) and nitrate at 50° for ten minutes.

Reynolds and Sutcliffe[c] found that dilute nitric acid free from nitrous has no oxidizing action on brucine and that when the reaction failed, it could be started by the addition of a minute amount of sodium nitrite—for example, 0.5 cc of 1/1,000 solution. When nitric acid of sp. gr. 1.42 was employed, the reaction never failed to occur satisfactorily at ordinary temperatures from 14° to 25° in ten minutes, but higher temperature or prolonged action is liable to cause decomposition and loss of strychnine.

Gordin's original method[d] directs the use of nitric acid of sp. gr. 1.42. As the method is incorporated in the Pharmacopœia the official nitric acid (sp. gr. 1.40) is specifically required. The difference of about 4 per cent in content of absolute nitric acid may be immaterial, but if the presence of a certain amount of nitrous acid is essential the directions require revision.

The Pharmacopœia in the purity rubric of nitric acid does not include a test for nitrous acid. Krauch[e] mentions the reduction of potassium permanganate by nitric acid as an indication of the presence of hyponitric or nitrous acid and states that owing to the tendency to decompose they are nearly always present in the strong acid.

According to Silberrad[f] strong solutions of nitric acid are only with difficulty freed from traces of nitrous acid. Reynolds and Sutcliffe were able by the use of urea and barium or sodium peroxid to so completely free fairly strong solutions of nitric acid from nitrous that they did not react with brucine, but never succeeded in doing this with a 1.42 sp. gr. nitric acid. They also noted that the permanganate reaction is not so delicate a test for nitrous acid in nitric as the brucine reaction.

It seems probable that nitric acid of sp. gr. 1.42 is more likely to contain nitrous acid than the pharmacopœial acid of sp. gr. 1.40, but until the invariable presence of nitrous acid in the former shall be established it evidently is advisable to direct the addition of a proper amount of sodium nitrite in the determination of strychnine in nux vomica by the nitric acid method.

The nitric acid employed in the experiments in the drug laboratory had a specific gravity of 1.4041 at 20°, and at the time of its receipt, some three months before, had failed to react for nitrous acid with the permanganate test. The irregularity of the nitrating action with this acid suggested that some impurity might be responsible for the slight reduction necessary to start the reaction, but no such agency was discovered. The most probable impurity seemed to be traces of solvent remaining in the alkaloidal residue.

The results by Method II (Panchaud's titration method) are reasonably concordant. In computing the titration results the factor 0.03615 (the mean of brucine and strychnine) was used. But as the results by Method I show that the total alkaloidal matter

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[a] Analyst, 1905, *30:* 261.

[b] Pharm. J., 1906, *77:* 83.

J. Soc. Chem. Ind., 1906, *25:* 512.

[d] Arch. Pharm., 1902, *240:* 641.

[e] Krauch. Testing of Chemical Reagents, 3rd ed., p. 186. Translated by Williamson and Dupré.

[f] J. Soc. Chem. Ind., 1906, *25:* 156.

contains about 40 per cent instead of 50 per cent of strychnine, the true factor is 0.03675 and the true average titration result 2.85 per cent, instead of 2.81 per cent total alkaloid.

In comparing the volumetric with the gravimetric results the different directions in Method II for drying the total alkaloids before weighing should be noted. It would perhaps be unsafe to assume that drying to constant weight in a desiccator would dehydrate the brucine as completely as drying to constant weight at 105°, which is directed in Methods I and III. Schmidt[a] states that crystallized brucine containing 4 molecules of water loses part of its water of crystallization at ordinary temperatures and all of it in vacuo over sulphuric acid or on heating to 100°.

The end reaction with hematoxylin as in "Ipecac" (II) was found not to be as sharp as is desirable, though not considered seriously objectionable. Method III, like the corresponding total extraction methods for cinchona and ipecac, gave too variable results to be entirely satisfactory for purposes of control. Like cinchona, nux vomica is a difficult drug to exhaust, and it is possible that in some instances, notwithstanding the test with Mayer's reagent, the marc was not entirely extracted. The thoroughness of the shaking-out process was not directed to be tested, and in this slight losses may have occurred.

Mr. Wiley. The subject of drugs will probably be of increasing interest to agricultural chemists in the future and especially to this association. There is a decided tendency to modify State laws as regards their general provisions in respect of foods and drugs to correspond with the provisions of the National law. This will bring to the State officials, who in many cases consider only foods, the similar work in regard to drugs, and as much of this work is done by experiment station chemists, the drug work will come largely to the same analysts. Everything relating to drugs, therefore, and especially methods for their examination, has a greater interest in this association than ever before. The Bureau of Plant Industry also is endeavoring to introduce into this country a great many drug plants not previously grown here, and in this way all chemical problems related to the production and assaying of drugs will come more directly in touch with the work of the agricultural chemist, whereas heretofore they have been considered principally by the pharmaceutical chemists. From both points of view, therefore, this section of the work is of great and increasing importance.

Mr. Kebler. Although some progress has been made in the cultivation of drug plants in this country, it is virtually impossible to compete with the imported products because of the low quality of the imported goods and the fact that they are produced by very low-priced labor. The food and drugs act, however, provides that if a product is recognized in the Pharmacopœia and does not comply with the standard set by this authority, while it may be imported, it must be marked to show its strength. This correct labeling of inferior products will enable the first-class products to compete on a fair basis.

[a] Lehrbuch der Pharmaceutischen Chemie, Part 2, p. 1398.

It should be noted that the chairman of the revision committee of the Pharmacopœia intends to issue a supplement of changes embodying corrections and defects in the standards that may be pointed out to him, and while this will not invalidate the Pharmacopœia as a standard as far as the National law is concerned, it may have a different effect in the States, and it might be well for State chemists to consider the matter and communicate with Professor Remington, of Philadelphia, who is in charge of the revision.

REPORT ON SOILS.

By J. H. Pettit, *Referee.*

In following out the instructions of the association on soil work this year, the referee sent to each chemist expressing a willingness to take part four samples of soil. Of these, sample No. 1 represents the level prairie land of the Lower Illinois glaciation in the southern part of the State. It is a gray silt soil with a rather stiff subsoil and lies too flat to give good surface drainage. Samples Nos. 2, 3, and 4 are from soil types included in the early Wisconsin glaciation occupying the northeast quarter of the State. No. 2 represents the gray silt soil of the timber land, No. 3 the brown silt soil of the gently rolling prairie land which is naturally well surface drained, and No. 4 the black clay loam which occupies the lower and poorly drained areas of the prairie and has received the wash of the higher, more rolling lands. Under the conditions found in the field these soils vary in productive power in the order named, sample No. 1 being the least productive, and not differing markedly from No. 2. In all fairness it must be stated that the phosphorus content of sample No. 1 shows that it represents the better phase of this type of soil, while that of sample No. 3 shows that it represents the poorer phase of the brown silt loam. For all of these soils 320,000 pounds may be taken as the weight of an acre-inch.

With these samples the following directions for analysis were sent out:

(*a*) Determine dry matter upon 5 grams of the air-dried soil by heating five hours in water oven.

(*b*) Weigh 400 grams of the air-dried soil into a 2½-liter flask, add 2,000 cc of distilled water, shake vigorously three minutes, let stand twenty minutes, and filter. Use an unglazed porcelain filter[a] if possible. If this is not convenient, filter through paper, shake up with 10 grams of carbon black[b] and refilter. Evaporate 1,500 cc of the clear solution to 25 cc, add 2 cc of concentrated nitric acid, neutralize with ammonia, make barely acid with nitric acid, add 15 cc of ammonium molybdate solution[c] and keep at 50° to 60° for two hours. Let stand overnight, filter, wash with 0.1 per cent ammonium nitrate solution until free of acid, and twice with cold water. Dissolve in a standard potassium hydroxid solution 1 cc of which contains 10.405 mg of potassium hydroxid and is equivalent to 0.25 mg of phosphorus. Titrate the excess with a nitric solution 1 cc of which is equivalent to 1 cc of the potassium hydroxid solution.

(*c*) Weigh 200 grams of the air-dried soil into a 2-liter flask, add 1,000 cc of distilled water, and treat as in (*b*). Evaporate 750 cc of the clear solution to 50 cc and determine potassium as in fertilizers.[d]

(*d*) Make a preliminary digestion of the air-dried soil in fifth-normal nitric acid at room temperature.[e] Weigh 220 grams of soil into a 2½-liter flask and add 2,200 cc of a solution of nitric acid of such strength that after allowing for the nitric acid neutralized by the soil, as shown by the previous digestion, there will be left 2,200 cc of fifth-

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[a] U. S. Dept. Agr., Bureau of Soils, Bul. 31, p. 12.

[b] Ibid., p. 16.

[c] U. S. Dept. Agr., Bureau of Chemistry, Bul. 46, p. 11.

[d] Ibid, p. 22.

[e] Ibid., p. 74, (b).

normal nitric acid solution. Digest five hours at room temperature, shaking every half hour. At the end of the digestion period shake and filter through a large folded filter, pouring the solution back onto the filter until it runs through clear.

Evaporate 1,000 cc of the filtrate to dryness, moisten with hydrochloric acid, bring to dryness again, bake five hours at 110°, take up with hydrochloric acid and water, filter, and wash. Evaporate filtrate and washings to about 25 cc, make alkaline with ammonia, and determine phosphorus as in (*b*).

Evaporate two 500 cc portions of the filtrate to complete dryness and determine total alkalies and potassium according to the official method[a], beginning with "dissolve in about 25 cc of hot water, add an excess of baryta water." Complete one of the two determinations according to this method, in the second introduce the modification suggested in the Journal of the American Chemical Society.[b]

The directions given under (*d*) for the determination of phosphorus are not exactly those followed by the Kentucky Experiment Station, some details being changed to make the results comparable with the rest of the work on phosphorus.

The following laboratories have reported some work in time for this report:

The Bureau of Soils, reported by G. H. Failyer.

The Virginia Experiment Station, reported by W. B. Ellett.

The Arkansas Experiment Station, reported by J. H. Norton.

The Minnesota Experiment Station, reported by H. Snyder.

The Michigan Experiment Station, reported by A. J. Patten.

The Kentucky Experiment Station, reported by S. D. Averitt.

The Illinois Experiment Station, reported by J. H. Pettit.

TABLE 1.—*Water-soluble phosphorus and potassium.*

[Parts per million in dry soil.]

Analyst.	Soil No. 1.		Soil No. 2.		Soil No. 3.		Soil No. 4.	
	P.	K.	P.	K.	P.	K.	P.	K.
S. D. Averitt, Kentucky[a]	1.1	.....	0.9	.....	0.9	.....	2.3	.....
G. H. Failyer, Bureau of Soils, Washington, D. C.[a]	2.0	23.0	2.0	11.0	2.0	12.0	3.0	23.0
J. H. Norton, Arkansas[a]	[b] 0	27.5	[b] 5.0	34.0	[b] .1	32.0	[b] .4	42.5
J. A. Hummel, Minnesota[a]	1.7	40.3	.9	27.5	2.7	31.6	2.3	35.3
Doroethea Moxness, Michigan[a]	[b] 12.1	23.2	[b] 17.9	[b] 55.1	.....	[b] 46.7	[b] 21.2	50.1
J. H. Pettit, Illinois	1.0	.....	1.2	.....	1.1	.....	2.5	.....
	1.0	.....	1.2	.....	1.0	.....	2.5	.....
A. Ystgard, Illinois	.....	12.1	.....	10.9	.....	13.6	.....	14.2
	.....	12.5	.....	10.4	.....	12.8	.....	15.1
Average	1.4	23.1	1.2	18.8	1.5	20.4	2.5	30.0

[a] Duplicates not reported. [b] Not included in average.

Considerable variation is to be noted among the results of the different analysts, in some cases the supposedly poorer soils showing the larger amounts of phosphorus or potassium.

G. H. Failyer, of the Bureau of Soils, determined phosphorus and potassium upon these soils by the colorimetric as well as the gravimetric method. His results are given in Table 2.

[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 46, p. 75 (k).

[b] 1903, *25:* 496.

TABLE 2.—*Water-soluble phosphorus and potassium (Failyer).*

[Parts per million in dry soil.]

Soil No.—	Potassium.		Phosphorus.	
	Gravimetric method.	Colorimetric method.	Gravimetric method.	Colorimetric method.
1	23	22	2	1
2	11	16	2	1
3	12	16	2	1
4	23	20	3	2

It will be noted that the phosphorus results show some uniform differences while those for potassium do not. It should be stated perhaps that phosphorus controls the yield upon all of these soils in the field so far as the two elements under consideration are concerned.

TABLE 3.—*Phosphorus, soluble in fifth-normal nitric acid.*

[Parts per million in dry soil.]

Analyst.	Soil No. 1.	Soil No. 2.	Soil No. 3.	Soil No. 4.
S. D. Averitt, Kentucky (1)	15.0	8.0	5.0	158.0
S. D. Averitt, Kentucky (2)	[b] 22.0	[b] 15.0	[b] 10.0	[b] 175.0
S. D. Averitt, Kentucky (3)	18.0	10.0	5.7	158.0
S. D. Averitt, Kentucky (4)	18.0	11.0	6.0	158.0
S. D. Averitt, Kentucky (5)	14.4	7.4	4.4	165.5
S. D. Averitt, Kentucky (6)	14.0	7.4	4.8	162.0
W. B. Ellett, Virginia	13.4	5.8	3.6	155.5
W. B. Ellett, Virginia	12.9	6.1	2.8	154.5
J. H. Norton, Arkansas [a]	14.0	7.7	3.1	163.4
A. D. Wilhoit, Minnesota	10.6	5.7	3.6	145.6
A. D. Wilhoit, Minnesota	.....	5.6	.....	.....
J. A. Hummel, Minnesota [a]	16.7	9.7	6.4	157.1
Doroethea Moxness, Michigan [a]	[b] 31.7	[b] 15.2	[b] 25.5	167.4
J. H. Pettit, Illinois	14.4	7.8	4.8	165.4
J. H. Pettit, Illinois	14.6	7.8	4.8	166.0
Average	14.7	8.3	4.6	159.7

[a] Duplicates not reported. [b] Not included in average.

[NOTE.—Averitt, No. 1. Work done according to directions sent out: No. 3. Baking of residue omitted: No. 5. Baking omitted and phosphorus determined by Kentucky method.]

Table 3 shows in the main satisfactory agreement in the results reported. The relatively large amount of phorphorus given by this solvent in No. 4 is to be noted, and also the fact that the relative amounts of this element in the other three soils is directly opposite to their relative productive capacities.

It is to be regretted that so few reports were received on the potassium work.

TABLE 4.—*Potassium, soluble in fifth-normal nitric acid, by two methods.*

[Parts per million in dry soil.]

Analyst.	Soil No. 1.		Soil No. 2.		Soil No. 3.		Soil No. 4.	
	Official.	Modified.	Official.	Modified.	Official.	Modified.	Official.	Modified.
W. B. Ellett Virginia	99.2	95.9	130.0	142.9	141.7	132.9	236.0	230.7
W. B. Ellett Virginia	88.7	95.0	135.9	139.8	139.8	138.8	233.1	235.1
J. H. Norton, Arkansas [a]	113.0	.....	128.0	.....	[b] 188.0	.....	[b] 276.0	.....
J. A. Hummel, Minnesota [a]	95.5	.....	127.9	.....	135.5	.....	234.4	.....
Doroethea Moxness, Michigan [a]	89.3	[b] 79.0	[b] 107.9	[b] 97.0	[b] 120.8	123.4	[b] 189.1	[b] 187.0
A. Ystgard, Illinois	91.3	97.7	136.0	139.7	142.5	150.4	244.9	253.2
A. Ystgard, Illinois	96.1	94.5	133.8	137.1	139.8	145.9	249.9	250.5
Average	96.2	95.8	131.9	139.9	139.9	142.0	239.7	242.4

[a] Duplicates not reported. [b] Not included in average.

It is to be observed that in all cases the amount found is in proportion to the productiveness of these soils. It is to be further noted that in two of the three cases where results by both methods are reported the two methods give concordant results.

Comments of Analysts.

Andrew J. Patten: The water solutions were filtered by means of suction through a thick pad of asbestos in a Buchner filter. The acid solutions were filtered through paper. The low results for total phosphorus by fusion with sodium peroxid is probably due to an incomplete fusion, as in her desire to follow the method strictly, Miss Moxness was very careful not to bring the mixture to complete fusion, and this is thought to be the reason for the low result. She did not have time to duplicate this work and so verify this point.

S. D. Averitt: In regard to your instructions for the determination of phosphorus, I beg to offer two objections: (1) Our experience in this laboratory indicates that the prolonged baking before filtering from the silica is not only unnecessary and a loss of time but that it renders the subsequent solution and filtration more difficult; (2) after the addition of molybdic solution and keeping at 50° to 60° for two hours, the standing over night seems open to serious objection, on account of the probable precipitation of molybdic acid, especially if a large excess of molybdic solution has been added. In the first determinations under (*d*) aliquots corresponding to 100 grams of soil were taken, and in the second determination aliquots corresponding to 40 grams of soil only could be had, but the same quantity of molybdic solution was used in each case. Now, in Nos. 1, 2, and 3, in which the amount of phosphorus is small, the second determinations show a large increase over the first; in No. 4, in which the amount of phosphorus present is from ten to thirty times as great as in 1, 2, and 3, the increase relatively is not nearly so great.

Harry Snyder: I note that in the case of the soils that contain appreciably large amounts of phosphorus soluble in fifth-normal nitric acid reasonably concordant results are secured, and in the case of soils with small amounts the agreement between the work of the two analysts is approximate. The difference is, I think, due to the fact that the end point in the titration is not as perfect as could be desired, and one analyst possibly carries the titration further than the other. In the case of large amounts of phosphorus this does not appear to affect the results appreciably as in the presence of small amounts.

Methods for the Determination of Total Phosphorus.

Directions for determining the total phosphorus by a sodium peroxid method to be compared with the usual alkali fusion method were also sent out. According to these directions, for the sake of greater accuracy, it was suggested that a larger amount of material be used than that suggested in our paper on the method presented last year. Later it was found that the changes made necessary by this modification affected the method fundamentally, giving much lower results and making the method cumbersome. Accordingly these directions and the results obtained thereby are omitted from this report.

The four samples were run for total phosphorus in the Illinois laboratory, however, by the following method:

Weigh 10 grams of sodium peroxid into an iron or porcelain crucible and thoroughly mix with it 5 grams of the soil. If the soil is very low in organic matter, add a little starch to hasten the action. Heat the mixture carefully by applying the flame of a Bunsen burner directly upon the surface of the charge and the sides of the crucible until the action starts. Cover crucible until reaction is over and keep at a low red heat for fifteen minutes. Do not allow fusion to take place. By means of a large funnel and a stream of hot water, transfer the charge to a 500 cc measuring flask. Acidify with hydrochloric acid and boil. Let cool and make up to the mark. If the action has

taken place properly there should be no particles of undecomposed soil in the bottom of the flask. Allow the silica to settle and draw off 200 cc of the clear solution.

Precipitate the iron, alumina, and phosphorus with ammonium hydroxid; filter, wash several times with hot water, return the precipitate to the beaker with a stream of hot water, holding the funnel over the beaker, and dissolve the precipitate in hot hydrochloric acid, pouring the acid upon the filter to dissolve any precipitate remaining. Evaporate the solution and washings to complete dryness on a water bath. Take up with dilute hydrochloric acid, heating if necessary, and filter out the silica. Evaporate filtrate and washings to about 10 cc, add 2 cc of concentrated nitric acid, and just neutralize with ammonium hydroxid. Clear up with nitric acid, avoiding an excess. Heat to 40° to 50° on water bath, add 15 cc of molybdic solution, keeping at this temperature one to two hours. Let stand over night, filter, and wash free of acid with a one-tenth per cent solution of ammonium nitrate and, finally, once or twice with cold water. Transfer filter to beaker, and dissolve in standard potassium hydroxid (1 cc=0.2 mg P), titrate the excess of potassium hydroxid with standard nitric acid, using phenolphthalein as indicator.

These details differ but slightly from those presented a year ago. The method was checked by the alkali-carbonate method, and Table 5 gives the results obtained.

TABLE 5.—*Total phosphorus sodium-peroxid and alkali-carbonate fusion methods (Illinois station).*

[Parts per million in dry soil.]

Soil No.	Sodium-peroxid fusion.	Alkali-carbonate fusion.
1	487.8	492.9
2	437.1	432.0
3	477.6	469.4
4	859.3	846.9

In November, 1905, practically the same directions were sent to a number of the members of this association who had consented to test the method. With these were sent two samples, one of soil and the other of the same soil to which rock phosphate had been added, so that the percentage of phosphorus in the mixture was 0.080. Table 6 contains the results of this work.

TABLE 6.—*Total phosphorus, sodium-peroxid fusion method (cooperative work).*

[Per cent in air-dried soil.]

Analyst.	Soil.	Soil plus rock phosphate.
A. Ystgard, Illinois	0.037	0.081
R. Harcourt, Canada	.036	.060
A. M. Peter, Kentucky	.046	.086
B. W. Kilgore, North Carolina	.046	.081
R. J. Davidson, Virginia	.038	.082
J. W. Ames, Ohio	.038	.071

From the results obtained this year and from others which have come under his observation, the referee does not recommend further work on water-soluble plant food, but would suggest rather that methods for the rapid determination of the total amount of the plant-food elements present be investigated, in order that we may thereby determine systems of extensive farming which may be applied over longer periods. In addition to this, further study should be made of some weaker solvent—fifth-normal nitric acid seems to be desirable—in order that we may thereby obtain some idea of the amount of the plant-food elements which may be obtained in shorter periods, and thus of the treatment necessary for intensive cropping of the land. Accordingly your referee would make the following recommendations:

RECOMMENDATIONS.

It is recommended—

(1) That the fifth-normal nitric-acid digestion method be further studied, both by correcting for the basicity as shown by a previous digestion and without such correction.

(2) That the sodium-peroxid fusion method for total phosphorus be given further trial and that this be compared with the alkali-carbonate fusion method.

(3) That the modified J. L. Smith method for total potassium presented at this meeting be further tested.

(4) That line 30 under "1. Preparation of sample," page 71, Bulletin No. 46, be changed from "openings one-half millimeter in diameter" to "openings one millimeter in diameter," and that "passed through a sieve of one millimeter mesh" be omitted from line 1 under (h) page 74, Bulletin No. 46.

(5) That the "Determination of volatile matter," page 72, Bulletin No. 46, be replaced by the "Determination of total organic carbon." (J. Amer. Chem. Soc., 1904, *26* : 1640.)

(6) That the "Determination of manganese," page 73, Bulletin No. 46, be omitted.

(7) That under (k), page 75, Bulletin No. 46, mark the official method "(a)" and insert the following:

B. OPTIONAL PROVISIONAL METHOD.

Proceed as in (a) through "let stand a few minutes in the water bath" and complete as follows:

Filter into a beaker, add a drop or two of hydrochloric acid and 1 cc of ammonium sulphate (75 grams to 1 liter), digest several hours on water bath, and filter into a tared platinum dish. Evaporate to *complete* dryness, heat to full redness, add 1 gram of powdered ammonium carbonate, expel by heating, cool, and weigh the sulphates of sodium and potassium. Determine potassium in the usual manner.

DETERMINATION OF TOTAL POTASSIUM IN SOILS.

By J. H. PETTIT and A. YSTGARD.

The following method is to be used for total potassium only and not for total alkalis. The well-known ammonium-chlorid and calcium-carbonate fusion, devised by J. Lawrence Smith,[a] is used. The fused mass is transferred to a porcelain dish, slaked with hot water, finely ground with an agate pestle, and transferred to a filter. After washing free of chlorids, the filtrate and washings are concentrated in a Jena beaker to about 20 cc and filtered. Filtrate and washings are slightly acidified with hydrochloric acid, concentrated in a platinum dish, and 1½ cc of a platinic chlorid solution (10 cc contains 1 gram of platinum) added where 1 gram of soil has been used. This is then evaporated to a sirupy consistency as usual and washed with 80 per cent alcohol and ammonium chlorid solution.

In Table 1 are given the results obtained upon five soils, first, when all calcium was removed as in the regular J. L. Smith method; second, when part of the calcium was removed by one precipitation with ammonium carbonate; and third, when no calcium was removed except that thrown out upon evaporating as indicated in the method described above.

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[a] Fresenius's Quantitative Analysis, p. 426.

TABLE 1.—*Total potassium determined by the Smith method and modification.*

Serial number.	All calcium removed (Smith).	Bulk of calcium removed by one precipitation.	No calcium removed.
	Per cent.	*Per cent.*	*Per cent.*
1263	1.731	1.716	1.736
1264	1.794	1.781	1.785
1265	1.843	1.818	1.840
1266	1.853	1.847	1.848
1267	2.064	2.038	2.037

With the Smith method without the removal of lime one man can easily make ten determinations on the average in a day of eight hours. Table 2 contains the results in duplicate obtained upon a number of soils.

TABLE 2.—*Potassium determinations in duplicate by the J. L. Smith method as modified by the authors (without removal of lime).*

Soil No.	Potassium (K).		Soil No.	Potassium (K).	
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
480	1.235	1.240	780	1.543	1.549
481	1.295	1.290	781	1.488	1.497
482	1.232	1.248	782	1.563	1.563
483	1.296	1.296	783	1.594	1.633
484	1.362	1.385	784	1.578	1.589
485	1.353	1.353	785	1.560	1.560

REPORT OF COMMITTEE ON REVISION OF METHODS.

The President called for the report of the committee on the revision of methods and the secretary asked permission to explain the appointment and purpose of the committee before the report was submitted.

Mr. WILEY. The association at the last meeting urged the secretary to issue a revised edition of Bulletin No. 46 on methods of analysis, instructing him to insert such changes as had been authorized by the association since the issuance of the methods in 1899 and make such verbal changes as were necessary to insure uniformity. With this end in view a study was made of the methods and the additions thereto by a committee composed of the chiefs of laboratories of the Bureau of Chemistry, from which it appeared that the revision as contemplated was not practicable for the following reasons:

The growth in the work, and the far-reaching changes and additions made since the issuance of the methods of analysis in 1899 and of the provisional methods of food analysis as Bulletin No. 65 in 1902, and the overlapping of these methods in many instances made it impossible to prepare a satisfactory revision without entirely rearranging the methods and consolidating these two bulletins. It was deemed wise therefore in the interests both of efficiency and of economy not to publish a partial revision prior to this convention but to ask the president to appoint a committee of the association to make a complete revision and submit it to the association for approval. This has been done, and the committee which has been at work previous to this meeting is now ready to report.

In partial compliance with the instructions of the association Circulars 28, 29, and 30 have been issued from the Bureau of Chemistry, giving the authorized revision

of the provisional methods for the determination of food preservatives, and the changes in and additions to Bulletins 46 and 65, respectively, since those reports were issued.

Mr. Haywood, chairman of the committee on the revision of methods submitted the following report, together with the manuscript of the revised methods:

The committee recommends that their report as submitted be provisionally accepted by the association for final adopton at the next meeting and that provision be made to supply the members of the association with copies for the purpose of criticism, before the next meeting, which criticism shall be submitted to the secretary in time for sufficient consideration before the meeting in 1907.

A number of minor recommendations submitted for the guidance of the secretary in editing the revision and insuring uniformity of expression were also submitted by the committee. The more important of the recommendations are as follows:

RECOMMENDATIONS OF REVISION COMMITTEE.

It is recommended that—

(1) A table of atomic weights be inserted.

(2) The secretary shall see that the methods are definitely designated either by the name of the originator or by some prominent reagent used in connection with them, especially where there are a number of methods for the same determination.

(3) All the methods be published in one bulletin.

(4) All weights and measures be expressed according to the metric system.

(5) The word "water" whenever used without qualification means distilled water; call attention to this in some prominent place in the bulletin.

(6) The strength of strong alcohol be expressed uniformly either as 95 or 96 per cent; dilute alcohols to be expressed both in percentage strength and specific gravity.

(7) Kröber's table for pentosans be inserted.

(8) Describe Volhard's method for chlorin under ash.

(9) Certain methods for insecticides be made provisional by the association.

(10) The Ruffle and soda-lime methods be dropped as official methods.

(11) The heading "Infants' and invalids' foods" be dropped.

(12) Under "Distilled liquors, Detection of methyl alcohol," the removal of acetaldehyde by Prescott's method be dropped; under same heading drop the S. P. Mulliken method for the removal of formaldehyde.

(13) The methods under "Dairy products" for the determination of casein monolactate and casein dilactate be dropped.

(14) Under "Flavoring extracts" the phenylhydrazin hydrochlorid method be dropped.

(15) The first method for the approximate quantitative estimation of saccharin be dropped.

(16) Methods for cocoa and chocolate be inserted as provisional.

(Signed) J. K. HAYWOOD, *Chairman.*
J. P. STREET.
F. W. WOLL.
J. H. PETTIT.
L. M. TOLMAN.
F. P. VEITCH.
A. L. WINTON.

On motion by Mr. Patrick the provisional method known as the Waterhouse test, for the detection of oleomargarin and renovated butter, was also dropped from the revised methods.

Mr. Wiley, referring to the main recommendation in regard to the distribution of the revision of the methods for criticism, called attention to the fact that so extensive a piece of printing could hardly be done for temporary use only, and asked for an opinion in regard to the changes that would be necessary before adoption. Mr. Haywood replied that as far as the committee was concerned their action was final and it was hoped that only minor corrections would be made.

With this understanding the report of the committee was adopted by the association, and upon motion by Mr. Bigelow the committee on revision of methods was continued for another year.

REPORT OF COMMITTEE ON NOMINATIONS.

Mr. Woods, chairman of the committee on nominations, presented the following report:

For president, Mr. J. P. Street, of New Brunswick, N. J.; for vice-president, Mr. Harry Snyder, of St. Anthony Park, Minn.; for secretary, Mr. H. W. Wiley, of Washington, D. C.; as additional members of the executive committee, Mr. B. B. Ross, of Auburn, Ala., and Mr. B. L. Hartwell, of Kingston, R. I.

The secretary was instructed to cast a unanimous vote for the officers nominated.

THIRD DAY.

FRIDAY—MORNING SESSION.

REPORT ON INORGANIC PLANT CONSTITUENTS.

By W. W. Skinner, *Referee.*

The work for this year has been confined to an investigation of sulphur and phosphorus found in plant materials, and the amounts of these substances remaining in the ash as obtained by various methods. The two materials selected for the work were cotton-seed meal (sample A), and white mustard-seed meal (sample B).

Total sulphur was determined by the peroxid method, and also by the absolute or combustion method (proposed by Sauer[a] and modified by Tollens and Barlow[b]) the results by the two methods agreeing fairly well. The results by the peroxid method are so entirely satisfactory, and the method has been given such a thorough test, that the referee recommends that this method for total sulphur, which is now provisional, be adopted by the association as an official method.

The results by the combustion method are interesting and it is believed that further investigation of the volatile and nonvolatile products obtained by this method may throw considerable light upon the vexing problem of how best to consider those so-called inorganic constituents which are partially or wholly lost in the ordinary methods of ashing plant substances. It is therefore recommended that particular attention be devoted by the referee for next year to this line of investigation.

Two years ago the association voted to substitute for "ash" the title of "inorganic plant constituents," which to the referee seems unfortunate as it leads to much confusion of terms. In our methods for the proximate analysis of foods and feeding stuffs, we have a distinct separation known as ash, yet nominally we have no methods for its analysis, unless "ash" is to be considered synonymous with "inorganic plant constituents." To the referee it seems that there is ample room for work upon ash, meaning thereby the residue obtained by ignition of organic materials in air or in oxygen, under approved and standard conditions, in addition to the investigation of the so-called inorganic plant constituents, some of which are volatilized, in part at least, by one of the above methods of combustion.

The following tables and discussion show the nature of the work for the year. Five chemists signified their intention of collaborating in the work and samples were sent to each in March, but no reports upon the samples have been received. The results are therefore confined to those obtained by the referee and one collaborator in the Bureau of Chemistry.

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[a] Zts. anal. Chem., 1873, p. 32.

[b] J. Amer. Chem. Soc., 1904, *26:* 341.

TABLE 1.—*Ash, sulphur (SO_4), and phosphorus (PO_4) in moisture-free cotton-seed meal (A) and mustard-seed meal (B).*

Method.	Analyst.	Ash.		Sulphur (SO_4).		Phosphorus (PO_4).	
		A.	B.	A.	B.	A.	B.
		Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Ordinary ashing	W. W. Skinner			0.17	0.33	.....	2.01
	C. Goodrich	.....	.....	.13	.30	4.48	2.04
	C. Goodrich	7.54	4.35	.....	.....	.....	.....
		7.57	4.33	.....	.....	.....	.....
Ashing with calcium acetate.	W. W. Skinner			.37	1.91	4.56	2.07
	C. Goodrich	.....	.....	.38	1.84	4.51	2.07
	C. Goodrich	7.76	5.67	.....	.....	.....	.....
		7.74	5.63	.....	.....	.....	.....
		7.67	4.19	1.64	4.24	4.55	2.04
Combustion method	W. W. Skinner	7.61	4.36	1.61	4.06	4.38	1.87
		7.53	4.19	.....	4.36	.....	.....
		7.55	4.29	.....	.....	.....	.....
Peroxid method	W. W. Skinner	.....	.....	1.73	4.37	4.49	1.96
		.....	.....	1.74	4.43	4.54	1.94
	C. Goodrich	.....	.....	1.69	4.33	4.53	2.01
		.....	.....	1.67	4.34	4.56	1.93

TABLE 2.—*Volatile and nonvolatile sulphur (SO_4) determined by the combustion method on moisture-free material.*

Sample.	Volatile sulphur.	Nonvolatile sulphur.	Total sulphur.
	Per cent.	*Per cent.*	*Per cent.*
A	1.62	0.02	1.64
	1.56	.05	1.61
B	4.11	.13	4.24
	3.79	.27	4.06
	4.15	.21	4.36

DISCUSSION OF RESULTS.

Ash in the two samples was determined by three methods:

(1) The ordinary method by charring, extracting with water, igniting the residue, adding the extracted matter, evaporating to dryness, etc.
(2) By igniting with a known quantity of calcium acetate.
(3) By combustion in oxygen.

A very close agreement is noted in the results for ash in samples burned in air and in oxygen. The sulphur in the ash obtained by these two methods is also fairly comparable. The volatile sulphur determined by the combustion method added to the sulphur remaining in the ash obtained by this method gives for total sulphur, figures comparable with total sulphur obtained by the peroxid method; the averages on samples A and B, respectively, are 1.49 per cent against 1.56 per cent, and 3.97 per cent against 4.11 per cent. Comparing the sulphur in the ash obtained by the usual method of ashing with the total sulphur obtained by the peroxid method a loss is noted of 91.2 per cent in the case of sample A and 92.7 per cent in the case of sample B. Practically all of the phosphorus remains in the ash, only traces being volatilized when proper precautions are exercised to prevent too high a temperature and fusion of the ash.

RECOMMENDATIONS.

It is recommended:

(1) That the peroxid method for total sulphur be adopted as official.

Peroxid method.—Place from 1.5 to 2.5 grams of material into a nickel crucible of about 100 cc capacity and moisten with approximately 2 cc of water. Mix thoroughly, using a nickel or platinum rod. Add 5 grams of pure anhydrous sodium carbonate and mix. Add pure sodium peroxid, small amounts (approximately 0.50 gram) at a time,

thoroughly mixing the charge after each addition. Continue adding the peroxid until the mixture becomes nearly dry and quite granular, requiring usually about 5 grams of peroxid. Place the crucible over a low alcohol flame (or other flame free from sulphur) and carefully heat, with occasional stirring, until contents are fused. (Should the material ignite the determination is worthless.) After fusion remove the crucible, allow to cool somewhat, and cover the hardened mass with peroxid to a depth of about 0.5 cm. Heat gradually, and, finally, with full flame until complete fusion, rotating the crucible from time to time in order to bring any particles adhering to the sides into contact with the oxidizing material. Allow to remain over the lamp for 10 minutes after fusion is complete. Cool somewhat. Place warm crucible and contents in a 600-cc beaker and carefully add about 100 cc of water. After violent action has ceased wash material out of crucible, make slightly acid with hydrochloric acid (adding small portions at a time), transfer to a 500-cc flask, cool, and make to volume. Filter and take a 200-cc aliquot for determination of sulphates by precipitating with barium chlorid in the usual manner.

(2) That the combustion method (i. e., the Sauer-Tollens-Barlow method) for determining volatile inorganic plant constituents be further investigated.

Mr. Wiley. It seems to me that the referee on inorganic plant constituents should not only study the proposed methods of analysis but should also consider the question, What is ash? The question arises, Is sulphur in combination an inorganic constituent? If it is, then nitrogen in inorganic compounds is an inorganic constituent also, and the same is true of every one of the elementary substances. The propriety of determining total sulphur in plants no one questions, but is it an inorganic constituent as determined by these methods? In my opinion, ash is the residual matter which remains after ordinary combustion of substances in the atmosphere, conducted in such a manner as to avoid loss by volatilization of the real ash constituents, and to secure under proper forms as complete a combustion of the carbon as possible. When incineration is conducted in that way a very large part, sometimes all, of the organic sulphur escapes detection and the same is true, to a large extent, of phosphorus. Therefore it appears that only the organic sulphur and phosphorus that can be fixed with the natural bases present before or during combustion can claim any place in the ash. It is very important in these studies that a clear distinction be made between the term "ash" as generally defined and the total sulphur, phosphorus, or other substances which may be present in inorganic form. The issue has become acute in some cases as to whether or not a determination of ash by the ordinary method really determines all of the ash. Some analysts are of the opinion that the ash should include the total sulphur and phosphorus in any form, and unless that is effected a real ash determination is not made. I do not share that opinion, simply from the analytical point of view, but since these differences of opinion exist it seems advisable that the association instruct the referee for the coming year to take up the question, "What is ash?"

REPORT OF COMMITTEE B ON RECOMMENDATIONS OF REFEREES.

By E. B. Holland, *Chairman.*

(1) Medicinal Plants and Drugs.

It is recommended:

1. That the present provisional method for the assay of opium products be made official. [Proceedings, 1905, Bul. 99, p. 162; U. S. Pharmacopœia, eighth revision, p. 329, with additions.]

Referred to the referee for 1907 for recommendation and final action by the association.

2. That the present line of work be continued by the referee on medicinal plants and drugs.

Adopted.

(2) Foods and Feeding Stuffs.

It is recommended:

1. That the König and modified König method for crude fiber be dropped. [See Proceedings, 1903, Bul. No. 81, p. 38.]

Adopted.

2. That the slightly modified Ellett-Tollens method for methyl-pentosans be tested again next year by the association. [J. Landw., 1905, *53*, (1): 13.]

Adopted.

3. Upon motion by Mr. Peter the association voted to instruct the referee for 1907 to study the temperature and time of drying of ether extracts.

Passed.

(3) Dairy Products.

It is recommended:

1. That the method of double extraction be adopted as provisional for the determination of fat in condensed milk, the directions to be given as follows:

fat.

Extract the solid residue of about 5 grams of a 40-per cent solution with ether in the usual manner; dry, leave tubes in a dish containing 500 cc of water or more, for two or three hours; dry, extract again for about five hours, and determine fat as under milk. [Bul. 46, p. 54.]

Adopted.

2. That the Gottlieb method [Landw. Versuchs. Stat., 1892, *40:* 1] be made provisional for the determination of fat in milk.

Referred to referee for 1907 for further recommendation.

3. That the conversion factor for protein in milk and dairy products be changed to 6.38 throughout the methods.

Referred to committee on unification of terms for reporting analytical results.

4. That the study of methods of analysis of condensed milk be continued with special reference to the determination of lactose and sucrose in the sweetened product.

Adopted.

(4) Sugar.

recommendations pending from 1905.

The following recommendations are made in regard to questions referred from 1905 for action [see Proceedings, 1905, Bul. 99, pp. 18–25, p. 155; Circular 26, p. 5]:

Chemical methods.

1. That the methods selected by the international committee for unifying sugar analysis, now provisional, be made official with the exception of paragraph 7, which should be eliminated, and paragraph 8, upon which action should be deferred. [See Proceedings, 1902, Bureau of Chemistry Bulletin No. 73, p. 58.]

Adopted.

2. That action upon recommendations 3 and 4 be deferred until 1907. These recommendations are as follows:

3. That method (*a*) for the determination of copper in the cuprous oxid precipitate, requiring reduction in hydrogen [see Bulletin No. 46, p. 37], be dropped as an official method of this association.

4. That methods (*c*) and (*d*) for the determination of copper in the cuprous oxid precipitate, requiring the electric deposition of the metal [see Bulletin No. 46, p. 38], be dropped as official methods of the association.

Action deferred as recommended.

3. That action for the adoption of Low's thiosulphate method for determining copper in the cuprous oxid be deferred until the original method and its modification has been compared by the association.

Adopted.

Molasses methods.

Of the five recommendations deferred from 1905 for action, No. 1 is covered by recommendation No. 3 under general recommendations on sugar, 1906, which follows, while action on Nos. 2, 3, 4, and 5 is deferred until further cooperation is obtained from interested chemists. [See Circular 26, p. 5, or Bulletin No. 99, p. 24.

GENERAL RECOMMENDATIONS, 1906.

It is recommended:

1. That further work be done upon the comparison of moisture methods for molasses and massecuites before action be taken by the association.

Adopted.

2. That when increased accuracy is desired in the determination of reducing sugars in commercial products on account of the danger of contamination in the precipitated cuprous oxid, only such methods be followed as provide for a direct determination (electrolytic or volumetric) of the reduced copper.

Adopted.

3. That in the optical methods for the analysis of dark-colored massecuites, molasses, and other low-grade products, the normal weight of substance may be made to some multiple of 100 cc, according to the volume necessary for accurate polarization. This normal weight may be weighed out directly and made up to the desired volume, or taken from a solution prepared by dissolving a larger amount of the material (50 to 100 grams) with water to a definite weight or volume. The latter method is to be preferred with nonhomogeneous materials, such as massecuite, to secure greater uniformity of sample.

Adopted.

4. That in the estimation of sucrose by the gravimetric method the calculation by the factor 0.95 (Bulletin 46, p. 39, bottom line) be made only upon the reducing sugars estimated as invert sugar. In making this calculation, reducing sugars previously present which require to be subtracted must also be expressed as invert sugar.

Adopted.

5. Provisional: That reducing sugars in mixtures either before or after inversion may also be expressed as dextrose, in which case the calculation of the true percentages of sucrose and other sugars may be made by appropriate conversion factors and formulæ. [Browne, Analysis of Sugar Mixtures: J. Amer. Chem. Soc., April, 1906.]

6. Provisional: That for the estimation of dextrose, invert sugar, maltose, and lactose, under uniform conditions of analysis, the method and table of Munson and Walker be adopted provisionally by the association. [Munson and Walker, Unification of Method for Reducing Sugars: J. Amer. Chem. Soc., June, 1906.]

Upon the suggestion of the referee, action on recommendations 5 and 6 was deferred, since but little cooperative work had been done.

7. That the questions of the influence of the lead precipitate, and the use of hypochlorites, hydrosulphites, and other agents for decolorizing in optical analysis, and the use of clarifying agents before estimating reducing sugars, be investigated further before decisive action is taken by the association.

Adopted.

8. That the cooperation of sugar chemists not members of the association be invited, to secure a greater expression of opinion upon matters pertaining to improvement of analytical methods.

Adopted.

(5) Tannin.

1. The report of the referee on tannin was not received until after the report of Committee B had been made, but it was considered by the committee and a supplemental report made by Mr. Kebler in regard to the recommendation of the referee that "the tannin section of the Association of Official Agricultural Chemists abandon the appointment of referee and associate referee and omit supervision of the tannin method." The committee recommended that the tannin work of the association be continued, and the recommendation was adopted by the association.

2. Upon motion by Mr. Veitch the method on tannin submitted by the referee in 1905 [Bul. 99, p. 123], as revised by the committee on revision of methods, 1906, was adopted as a provisional method, the changes made by the committee being almost exclusively in manner of statement, etc.

In discussing the sugar recommendations Mr. Wiley made the following remarks: The recommendation that all polarizations be made at 20° C. must be interpreted to mean that when it is not practicable to maintain this temperature the results should be referred to it for correction. This is necessary because in commercial work the wide differences in temperature which occur result in enormous differences in polarization. As I showed some years ago, a difference of 1.25 per cent may be obtained on the same sugar by polarizing at different temperatures. The members of the association may recall that a legal battle was fought on this point on the ground that when Congress passed a law saying "as determined by polarization" the system of polarization then in commercial use was meant, in which no attention was paid to the temperature of polarization. The question was carried to the Supreme Court of the United States and the decision of the lower court sustained, namely, that the Secretary of the Treasury had absolute right to prescribe the regulations under which the polarization should be made, and to say that it must be made under the conditions obtaining when the law was passed was to bar scientific progress. Thus the principle was established that these corrections for temperature could be legally applied in commercial work.

Mr. Woll. I would like to bring up a matter of general interest. It seems only right that the association should take action in regard to the views expressed in the president's address, and to that end, Mr. President, I move that a committee of seven on the presidential address be appointed by the vice-president, to consider the questions discussed in the address and to make such recommendations as to an expression of the position of this association as in their judgment are deemed advisable.

The motion was carried.

REPORT ON PHOSPHORIC ACID.

By B. W. Kilgore, *Referee.*

Three questions were submitted by the association to the referees on phosphoric acid for investigation the past year, as follows:

(1) Methods for determining available phosphoric acid in Thomas or basic slag.
(2) Methods for determining iron and alumina in phosphates.
(3) Testing citrate solution.

Mr. McCandless, the associate referee, agreed to undertake the investigation of problems (2) and (3), leaving for our consideration methods for determining available phosphoric acid in slag. For four or five years we have been conducting field experiments with slag in comparison with other phosphates on three types of soil—red clay, sandy loam with red clay subsoil, and a sandy loam of the coastal plain section. The data are being tabulated, but are not ready for publication.

We also have samples of the slag which we propose to analyze by different methods for the purpose of comparing laboratory and field results. It is not possible, because of the incompleteness of the work, for us to submit a report with recommendations at this time, but it is our purpose to continue the investigation and report at a later date.

REPORT ON DETERMINATION OF IRON AND ALUMINA IN PHOSPHATES AND ON THE CITRATE SOLUTION.

By J. M. McCandless, *Associate Referee.*

The unusual amount of official work imposed upon the associate referee during the fertilizer season in Georgia made it impossible for him to send out instructions and samples for cooperative work, or to file a timely report with the secretary. Some work, however, has been done which promises well and may serve as a basis for careful study and comparative tests during the coming year. The two subjects which I proposed to investigate as associate referee on phosphoric acid were the methods for the determination of iron and alumina in phosphate rock, and the neutralization of the ammonium citrate solution. The following notes are offered on these subjects:

Mr. R. G. Williams, of the Georgia State laboratory, collaborated in the work on iron and alumina. We made a number of analyses of phosphate rock by various methods, chiefly the acetate and the Glaser methods, with their various modifications, with varying results, so that when the work was finished we were not sure of the actual percentages of iron and alumina in any of the samples. Evidently it was necessary to work on a solution containing known quantities and resembling a solution of rock phosphate as closely as possible. To that end a solution in hydrochloric acid was prepared, containing known quantities of chemically pure calcium carbonate, microcosmic salt, ammonia-alum, and iron wire.

From this solution the best results were obtained by the acetate method, as modified and described by Gladding, and by the original Glaser method. Both methods, however, involve the difficult washing of a gelatinous precipitate, and in both methods if a separation is made the alumina must be obtained by difference. From a consideration of the combining weights of the phosphates of iron and alumina, it was evident that the present commercial practice of dividing the weight of the mixed phosphates by two to obtain the percentage of oxids of iron and aluminum might be the cause of grave errors, and that any really scientific method of making the determination must involve the separation of the two metals in a state of purity.

In the endeavor to avoid the washing of the gelatinous precipitate an indirect method suggested itself. An aliquot of the phosphate solution in which the phosphoric acid had been carefully determined, was transferred to a 250 cc flask, precipitated by the the acetate method, and the solution made up to the mark, cooled, and filtered through a dry filter. An aliquot of this solution was then boiled down with excess of nitric acid until acetic acid was driven off, and the phosphoric acid carefully determined in the residue; the difference between the phosphoric acid in the original solution and in the acetate solution gave the phosphoric acid which had combined with the iron and aluminum. Some promising results were obtained in this way, but the method requires the utmost accuracy in the determination of the phosphoric acid. The iron being determined by a volumetric method, the alumina was of course easily calculated. The results, however, were not sufficiently uniform and the following method was finally decided upon, and is recommended, not only for its accuracy but for its rapidity and ease of manipulation. It is based upon Wöhler's observation, that aluminum phosphate may be separated from iron by means of sodium hyposulphite in a solution, slightly acid with hydrochloric and acetic acids. The details of the method are as follows:

Weigh out 2.5 grams of phosphate rock, dissolve in 25 cc of hydrochloric acid, make up to 250 cc, and filter off 100 cc through a dry filter, neutralize with ammonia, clear with hydrochloric acid, add 200 cc of water, 2 cc of concentrated hydrochloric acid, 10 grams of sodium thiosulphate, and 15 cc of acetic acid (specific gravity 1.04). Boil for fifteen minutes, filter on an ashless filter paper, and wash with ammonium nitrate solution. Ignite over a low flame until the filter paper is ashed and finally at a red heat. Weigh as aluminum phosphate containing 41.85 per cent of aluminum oxid. Determine iron in another portion of the original solution by the bichromate or other suitable volumetric method.

The following solutions were prepared: No. 1 to represent a rock containing 2.5 per cent of ferric oxid and 2.5 per cent of aluminum oxid; No. 2, 2 per cent of ferric oxid and 5 per cent of aluminum oxid; No. 3, 5 per cent of ferric oxid and 2 per cent of aluminum oxid; No. 4, 5 per cent of ferric oxid and 7 per cent of aluminum oxid. All of the solutions were prepared to represent a rock containing 35 per cent of calcium oxid and 31 per cent of phosphoric acid.

The results on alumina were 2.62 per cent found, *v.* 2.5 per cent present in No. 1; in No. 2, 5.10 *v.* 5; in No. 3, 2.15 *v.* 2; in No. 4, 7.14 *v.* 7. The precipitates agglomerated with the free sulphur on boiling, washed with ease, and the ignited residues were perfectly white and free from reddish color. The results obtained volumetrically on the iron also agreed closely with theory. In the case of sample No. 2 the usual method of dividing the weight of the mixed oxids, as obtained by the ordinary acetate method or by the Glaser method, by 2 would involve an error of nearly 1 per cent.

In the investigation as to the neutralization of the official solution of ammonium citrate my collaborator was Mr. Joseph Q. Burton, first assistant State chemist of Georgia. Chemists have long been dissatisfied with both the litmus and corallin tests for neutrality of the solution. The calcium-chlorid method only enables one to tell when a neutral point is reached at the expense of repeated tests and much trouble. The following method for making a neutral solution is based upon the fact that citric acid

may be titrated with accuracy by a standard solution of caustic soda or potash with phenolphthalein as indicator.

First determine the percentage of pure citric acid in the commercial article with standard caustic potash and phenolphthalein. Weigh out a suitable quantity, calculate the quantity of ammonia solution necessary to neutralize it, pour the somewhat diluted solution on to the crystals, and agitate until dissolved. Cool, and make up to a definite volume; the solution will have lost some ammonia from the heat and will be acid. Ascertain the quantity of ammonia in a measured volume by distillation with excess of normal caustic potash and titration of the distillate with standard acid. Then titrate the excess of normal potash in the retort and calculate the citric acid which was combined with the ammonia. Knowing the amount of citric acid and ammonia in the measured volume, calculate the quantity of ammonia necessary to neutralize the free citric acid. Add this quantity from a solution of ammonia of known strength, shake, and bring to a specific gravity of 1.09. Our experience shows that citrate solutions made neutral to litmus or corallin are generally decidedly acid.

Mr. Stillwell. The commercial chemists are constantly receiving importations of basic slag for analysis. I believe importers are guaranteeing the available phosphoric acid by the seiving method used at the California station, and I do not know what we are going to do as commercial chemists unless some action is taken by the association. I would urge that the referee recommend a method for the determination of available phosphoric acid in basic slag as soon as possible. Mr. McCandless spoke of the Gladding modification for the determination of alumina; do I understand that you get the iron and alumina together?

Mr. McCandless. In the acetate method they are precipitated together, but may be separated by treating with caustic soda or potash. Most of the chemists use the Glaser method.

Mr. Stillwell. We always report the iron and alumina separately.

Mr. McCandless. But your separation is made by means of caustic soda or potash. We found so much alumina in potash that the results were entirely unsatisfactory, and in the method proposed for the separation of iron and alumina it is easy to obtain chemically pure reagents.

Mr. Hand. We have used the following method in Mississippi with good results:

To the solution, prepared in the usual manner, add 8 grams of ammonium oxalate, heat nearly to boiling, neutralize cautiously with diluted ammonia, and add a few drops of dilute acetic acid to faint acid reaction. Place the beaker on a water bath for about two hours, filter, and wash. The calcium oxalate will be practically free of compounds of iron, alumina, and phosphoric acid. Concentrate the filtrate if necessary. Heat to 70° or 80°, and destroy the ammonium oxalate by electrolysis. The current should be passed until odor of ammonia has entirely disappeared. About 3.5 to 4 ampère hours are sufficient. The ammonium oxalate may be oxidized in an hour and a half. So far we have used only the lighting circuit, supplying current at 220 volts.

After dissolving the mixed precipitates we have a solution free of lime, containing nothing except probably a small amount of magnesia, to interfere with the

precipitation of the iron and aluminum phosphates, and in ordinary rocks these may be thrown out at once with ammonia after the addition of about 1 gram of ammonium phosphate. The ammonium phosphate should not be neglected. When properly carried out the method has given highly concordant results. Very good results may be secured also by destroying the oxalate by nitric acid and potassium chlorate after evaporating almost to dryness. This procedure, however, for obvious reasons, is not as satisfactory as the process employing the current. In presence of a considerable amount of magnesia the iron and alumina may be precipitated as in the acetate method. We have not had an opportunity of testing this method carefully, but propose to do so as soon as possible.

Mr. Veitch. The American Chemical Society has recently appointed a committee of five to study the determination of alumina and iron in phosphates, and this committee will be very glad to hear from all who are interested in this question as to their methods and to receive suggestions as to the lines of work to be followed. It seems to me that we must consider not only the methods for the determination of these substances, but also in what combinations they exist. Shall we determine total iron and alumina in phosphates, or exclude the sulphids of these bases in the analysis? This is a question of some commercial importance, and we would like to have the benefit of the experience of the commercial and manufacturing chemists in considering it.

I did a great deal of work on the thiosulphate method about five years ago and found it to be a most excellent method for the separation of alumina from iron in the form of phosphate. I found, however, that two precipitations would give practically theoretical results, while one was not sufficient, usually carrying down a little iron. I also doubt the accuracy of the method when solution is made in hydrochloric acid and alumina immediately precipitated without the removal of silica. The effect of fluorids must also be considered, and it is always necessary to wash with 5 per cent ammonium nitrate solution, as the aluminum phosphate is hydrolized by hot water, phosphoric acid being dissolved and passing into the filtrate.

Mr. McCandless. I have made some experiments in treating a number of samples of ground phosphate rock containing known quantities of iron sulphids with sulphuric acid of 1.53° specific gravity, and in no case did any of the iron sulphid go into solution. As it was not oxidized by the sulphuric acid, it would be unfair to introduce nitric acid into the solution, as iron sulphid does not affect the phosphate made from such a rock. It was also found that in separating the iron and alumina as phosphates and dividing by 2, a common practice, very inaccurate results may be obtained.

Mr. Mooers. I would like to say in this connection that the Tennessee phosphate contains a large amount of iron sulphid, and the chemists at Mount Pleasant use a dilute hydrochloric acid solution—about 1:1 strength usually. Some manufacturers have made to me

the same remark made by Mr. McCandless—that the iron and alumina sulphids do not affect the manufacture of phosphate.

The Assistant Secretary of Agriculture was presented by the president of the association and addressed the convention as follows:

ADDRESS BY ASSISTANT SECRETARY OF AGRICULTURE.

Gentlemen: I am very glad to meet with you and to have the opportunity of congratulating you upon the fact that your work in this association is leading to large things; of this there is every evidence. Your peculiar work makes much possible along the lines of the development of research, and it is also useful in the industries, in home making, and in promoting good living. It is also educational, especially in definitely educating the people at large concerning many things that relate to farming and the home life. You have evidence, which I know is very satisfying to you, of your good work in some of the matters that have become the subject of National legislation, especially the pure-food law, which has been largely promoted by this association. As the plans for the execution of this law go on it is plain that the good it is going to do will not only be economic, but also ethical. As Doctor Wiley says, it is going to have an effect in producing business honesty in this country, which will extend to our relations with foreign countries. The food question is one of the matters that have been neglected in this great Republic until affairs were in rather bad condition, but now we have taken hold of the matter and reorganized it. It is a great law.

I think the Department of Agriculture has reason to be proud that it has given support to this organization and helped it in its work. Not long ago the question arose as to whether the printing of the annual reports for other societies and this society should continue to be the general policy of the Department, and when a statement was made as to the relations of the Department to the work of the Association of Official Agricultural Chemists the correctness of the policy became plain. The arrangement you have had for the publication of your reports seems to have been very wise, and much good has been done and many things made possible that would not have been possible without such an arrangement.

Many difficult problems confront us in these technical questions and I know you all are disposed to meet them in a scientific spirit. When we have any differences among us it seems wise that we specify them, define the questions in regard to which we differ, and apply ourselves to the solution of such definite questions by specific methods.

I am glad to be with you.

Vice-President Street reported that the following committee on the president's address had been appointed: Messrs. Woll, Davidson, Penny, Peters, Ross, Van Slyke, and Winton. [Mr. Winton withdrew from the committee subsequent upon his resignation from the Connecticut station, and Mr. J. G. Lipman of the New Jersey station was appointed to fill the vacancy.]

REPORT ON TANNIN.

By H. C. Reed, *Referee.*

Among the matters referred to the consideration of the referee for 1906 are the following suggestions made by a committee of the American Leather Chemists' Association:

(1) That the executive committee of the Association of Official Agricultural Chemists appoint a special committee on recommendations for the tannin section and that

the association appoint the same referee and associate referee on tannin as are appointed by the American Leather Chemists' Association.

(2) That the Association of Official Agricultural Chemists abandon the appointment of a referee and associate referee on tannin and consequently omit for the present any supervision of the tannin methods.

As the reasons for these suggestions are not given in the report of last year's proceedings, the referee considers it wise to call attention to them, and in order to do this he presents herewith a copy of the original letter embodying such reasons.

NOVEMBER 17, 1905.

Dr. H. W. WILEY.

DEAR SIR: Confirming the conversation we had with you to-day, we herewith present our suggestions relative, first, to the probable action of the executive committee of the Association of Official Agricultural Chemists in the matter of appointing a special committee on recommendations for the tannin section and to the possibility of having the Association of Official Agricultural Chemists appoint the referee and associate referee that are appointed by our association; and, second, the inclination of the Association of Official Agricultural Chemists to abandon the appointment of referee and associate referee by your association and consequently omit for the present your supervision of the tannin method.

We would request that this be done with the view of having but one method of tannin determination, inasmuch as most of the members of the Association of Official Agricultural Chemists have no interest in the work, and, in reality, the work is being done almost entirely by members of the American Leather Chemists' Association, who can not become voting members of the Association of Official Agricultural Chemists and thereby protect their interests.

We would ask that action be taken in one of the two lines proposed, and would suggest that the latter proposition, being more acceptable to you, should receive the more favorable consideration.

We feel that our interest in the tannin method is of paramount importance, representing as we do practically all of the tanning interests of this country, and that two methods of analysis would be highly detrimental to commercial interests.

(Signed.) W. H. TEAS,
H. C. REED,
J. H. YOCUM,
Committee of the American Leather Chemists' Association.

In a letter addressed to the referee dated December 16, 1905, Doctor Wiley, secretary of the Association of Official Agricultural Chemists, says:

We are very appreciative of the extent and quality of the cooperative work done by the American Leather Chemists' Association, and shall hope that such collaboration may be continued. Many trade interests cooperate in this way in the official work to mutual advantage, but even a cursory examination of the constitution and the objects for which our association exists makes it plain that to coalesce completely with any trade association, however able in their investigations, would be to nullify the authority of the methods, this authority depending largely on the fact that they are adopted by official chemists acting from a purely disinterested standpoint. This is without any prejudice against either the fair-mindedness or ability of the trade chemists, but must necessarily be true when any special interests are involved. A neutral or disinterested opinion carries weight. The fertilizer interests, the food men, and the glucose manufacturers have all discussed their views, presented their methods, etc., in the association.

The present conditions have arisen, I think, from a misunderstanding of the conduct of the association, its interpretation of the terms "official" and "provisional" methods, and its policy as outlined in the constitution, and I believe that we can conduct the cooperative work on tannin in the future with mutual profit.

The referee would call attention to the fact that recommendations on tannin methods would be presented to the executive committee of the Association of Official Agricultural Chemists, approved by exactly the same body of chemists and representing the same interests as when the recommendations are considered by the American Leather Chemists' Association. This would mean that if trade interests entered into the matter at all they would have opportunity of so doing equally under the rulings of both associations with the advantage, if anything, in favor of the American Leather Chemists' Association, since in this body the recommendations would be

passed upon by those acquainted with the methods, which is not altogether the case with the executive committee of the Association of Official Agricultural Chemists.

During the past year many further reasons have appeared indicating the advisability of the abandonment of the tannin section by the Association of Official Agricultural Chemists. The American Leather Chemists' Association has been rapidly increasing in membership and has become recognized by the International Association of Leather Trades Chemists as the representative association in tannin investigation for this country. This is indicated in all the recent utterances of the Collegium, the official organ of the International Association of Leather Trades Chemists, where the American Leather Chemists' Association is now alone referred to and not the Association of Official Agricultural Chemists.

The past year has witnessed the publication of a monthly journal by the American Leather Chemists' Association, devoted to the interests of tannin work, and it is respectfully pointed out that such a desirable attainment could not result under the rulings of the Association of Official Agricultural Chemists.

Attention is also called again to the fact that, as stated in the letter of the committee of the American Leather Chemists' Association of November 17, 1905, members of the American Leather Chemists' Association can not become voting members of the Association of Official Agricultural Chemists and thereby protect their interests. Does it not seem quite unfair that recommendations made by a referee and backed by an association actively engaged in the work should be passed upon by a committee of which possibly only one member is by experience acquainted with the why and the wherefore of such recommendations? Moreover, the referee understands the impossibility, under the rulings of the Association of Official Agricultural Chemists, of the appointment of a committee on recommendations from other than active members of the association.

The advantage of having but one method of tannin determination is quite apparent, and with this in mind the referee determined, after mature deliberation, that it would be exceedingly unwise for him to submit a report upon tannin this year, which might conflict with the report of the referee of the American Leather Chemists' Association. Moreover, it is exceedingly doubtful whether more than a mere handful of analysts would have agreed to assist in the work of the Association of Official Agricultural Chemists under the circumstances.

The appreciation of the good offices of the Association of Official Agricultural Chemists is fully recognized, especially by the older members of the American Leather Chemists' Association, who have been referees and collaborated in the tannin work for the Association of Official Agricultural Chemists in the past, but the scope of work now embraced has become so large as to make the handling of it awkward under the rulings of the Association of Official Agricultural Chemists. In witness of this the referee quotes the following from Bulletin 99, United States Department of Agriculture, page 122.

[Note by the Editor.—The detailed reports of the several committees have been printed in full in the Shoe and Leather Reporter for November and December, 1905, and January, 1906, and abstracts of the report have appeared in Hide and Leather and in Leather Manufacturer for November and December, 1905. It is regretted that lack of space prevents the publication of the details of this valuable and exhaustive report in these proceedings, but it is only possible to present the outline of work and the recommendations and proposed official method as offered by the referee for ratification and final adoption in 1906.]

It is respectfully suggested that if "lack of space" prevents the publication of the referee's report on tannin then surely has the work of the tannin section outgrown the capacity of its being cared for by the Association of Official Agricultural Chemists.

However, the referee would, in closing, urge upon your body the advisability of adopting the recommendations embodied in the report of the referee of the American Leather Chemists' Association for this year, provided that it is not considered advisable to abandon the tannin section of the Association of Official Agricultural Chemists.

He feels, however, very strongly, and so recommends, that the tannin section of the Association of Official Agricultural Chemists abandon the appointment of referee and associate referee and omit the supervision of the tannin method.

Mr. Wiley. It is only fair that a statement of the case should be made from the agricultural chemist's point of view. The production of leather is undoubtedly an agricultural industry of the first magnitude, and tannins, considered both in connection with forestry and with leather making, are essentially agricultural products. We have received a great deal of help from the technical chemists engaged in the leather trade, of which we are very appreciative, and we have no doubt of their desire to do the right thing, but since they have thought best to disassociate themselves entirely from the work of this association and recommend that we discontinue the work, I am of the opinion that it is our duty as official agricultural chemists to continue independently the work of establishing official methods for the analysis of tannins, using such information from the reports of the American Leather Chemists' Association as enable us to be perfectly fair to the trade interests. While we should prefer that there should be complete unity of action as to methods, I, for one, would not feel that I could support the recommendation of the referee in this case.

Mr. Veitch. In addition to what Mr. Wiley has said, I would call attention to the fact that the time is coming when the examination of tanning materials will be of much greater interest to the association than formerly, as our raw tannin materials are decreasing very rapidly and increasing in price. I think, therefore, the growing of tannin material will become a profitable agricultural industry and the investigations looking to the discovery of new and available tannins and the increase of the tannin content in those materials which are now known will constitute an important line of work. Under the new food and drugs act there are a number of medicinal tannin compounds which, while not of great importance, must be considered. I should dislike to see the association give up this line of work, as it is more likely to grow in importance than to decrease.

The President. I will ask Mr. Veitch, who presented the report of the referee, to communicate this matter to the chairman of Committee B, who is absent.

Mr. Wiley. I hope the committee will consider what has just been said and that they will recommend that this association continue to conduct this line of work.

The referee on insecticides, Mr. George E. Colby, was not present, and reported by letter to the secretary that no cooperative work had been accomplished. The following paper was submitted by the referee, together with the recommendation that the methods previously studied be further investigated, with a view to their adoption as official:

DETERMINATION OF KEROSENE IN KEROSENE EMULSION BY THE CENTRIFUGAL METHOD.

By G. E. Colby.

The following preliminary results on kerosene emulsion are submitted in order that others may consider the subject and an official method be developed for the examination of this class of materials.

The method followed in the work here reported is as follows:

Six, 9, or even 18 grams, according to the strength of kerosene emulsion, are weighed and measured in cubic centimeters at 15.5° C. into a Babcock cream bottle, graduated to 35 or 50 per cent. To this add 3 or 4 cubic centimeters of strong sulphuric acid and twirl one minute in a Babcock machine; then add cold water and twirl again one minute; finally add water sufficient to bring the water to or above the zero mark in the neck of the Babcock bottle; read the cubic centimeters of kerosene obtained at 15.5° C. Calculate volume percentage of kerosene on cubic centimeters of elmusion used in the test.

Results on kerosene emulsions (sp. gr. 0.7820 at 15.5° C.) by the centrifugal method.

Description of sample.	Actual kerosene used.[a]	Kerosene (uncolored) obtained by Babcock method.
I. Kerosene emulsion[b]	66.6	66.8
		[a] 66.5
Ia. Same emulsion diluted 2.33 times (i. e., 3 gallons plus 4 gallons water)	28.5	28.7
Ib. Same emulsion diluted 7.6 times (i. e., 3 gallons made to 23 gallons)	8.6	8.7
II. Petroleum emulsion[c]	85.7	[a] 85.7
IIa. Same emulsion diluted 6 times original volume	14.2	14.3

[a] Specific gravity of kerosene at 15 5° C. determined and found to be 0.7820.
[b] Hubbard-Riley formula, p. 155, Spraying of Plants, Lodeman.
[c] Penny's formula No. 1, p. 23, Delaware Agr. Exper. Sta. Bul 75.

METHODS OF ANALYSIS OF LEAD ARSENATE.

By J. K. Haywood.

Methods of analysis of a large number of classes of insecticides have been gathered together and comparatively studied during the past six or seven years by the Association of Official Agricultural Chemists, but in this time no methods have been even suggested for a very important class of insecticides, i. e., lead arsenates which are now manufactured and sold by a number of firms in this country.

Lead arsenate is usually prepared by the action of lead acetate on disodium arsenate. By studying the resulting lead arsenate it was found that the following reaction was followed:

$$3\ Pb(C_2H_3O_2)_2 + 2Na_2HAsO_4 = Pb_3(AsO_4)_2 + 4Na(C_2H_3O_2) + 2H(C_2H_3O_2).$$

In case the crystallized varieties of lead acetate and disodium arsenate as they usually appear on the market are used the reaction is as follows:

$$3Pb(C_2H_3O_2)_2.\ 3H_2O + 2Na_2HAsO_4.\ 7H_2O = Pb_3(AsO_4)_2 + 4Na\ C_2H_3O_2 + 2HC_2H_3O_2 + 23H_2O.$$

However, some manufacturers prepare lead arsenate by the action of lead nitrate on disodium arsenate. A study of the resulting lead arsenate shows that the following reaction is followed in the main:

$$Pb(NO_3)_2 + Na_2HAsO_4 = PbHAsO_4 + 2NaNO_3,$$

although a very slight variation of the resulting compound from the theoretical composition of lead hydrogen arsenate would suggest that some unknown secondary reaction takes place to a small extent.

In case the crystallized variety of disodium arsenate as it appears usually on the market is used the following reaction is followed:

$$Pb(NO_3)_2 + Na_2HAsO \cdot 7H_2O = PbHAsO_4 + 2NaNO_3 + 7H_2O.$$

It will thus be seen that if the resulting lead arsenate were washed entirely clean of all impurities by the manufacturers it would be necessary to devise methods of determining only total lead oxid, total arsenic oxid, moisture, and soluble arsenic oxid (representing the solubility of the lead arsenate itself). However, the resulting lead arsenate is not washed perfectly clean of all impurities by the manufacturer, but is washed perhaps only once or twice or not at all and the remaining mother liquor removed by a filter press, so that in commercial samples sodium acetate or sodium nitrate are practically always present. Besides this a slight excess of lead acetate or lead nitrate used in making the lead arsenate will also be present, on account of insufficient washing, and in certain cases where sufficient soluble lead salt was not added to precipitate all arsenic a small amount of sodium arsenate might be present. This latter condition, however, has never been actually observed by the author in commercial samples.

It will thus be seen that in commercial samples not only is it necessary to determine moisture, total lead oxid, total arsenic oxid, and soluble arsenic oxid, but it is also necessary to determine soluble lead oxid and total soluble solids, which latter may, in a broad sense, be considered as the impurities present in the concentrated sample. It is the habit of the writer to state the results of the complete analysis of a sample of lead arsenate in the following way:

	Per cent.
Moisture	------
Total arsenic oxid	------
Total lead oxid	------
Soluble impurities (exclusive of soluble lead oxid and arsenic oxid)	------
Total	------
Soluble arsenic oxid	------
Soluble lead oxid	------

Methods of Analysis.

General directions.

In case the sample is in the form of a paste, as it usually is, dry the whole of it to constant weight at the temperature of boiling water and calculate the result as total moisture. Grind the dry sample (which will gain a small amount of moisture by so doing) to a fine powder and determine the various constituents as follows:

Moisture.—Weigh out 2 grams of the sample and heat in the water bath for eight hours or in the hot-air bath at 110° C. for five to six hours or till constant weight is obtained.

Total lead oxid.—Dissolve 2 grams of the sample in about 80 cc of water and 15 cc of concentrated nitric acid on the steam bath; transfer the solution to a 250 cc flask and make up to the mark. To 50 cc of the solution add 3 cc of concentrated sulphuric acid, evaporate on the steam bath to a sirupy consistency and then on the hot plate till white fumes appear and all nitric acid has been given off. Add 50 cc of water and 100 cc of 95 per cent alcohol. Let stand for several hours and filter off supernatant liquid, wash about ten times with acidified alcohol (water 100 parts, 95 per cent alcohol 200 parts, and concentrated sulphuric acid 3 parts) and then with 95 per cent alcohol till free of sulphuric acid. Dry, remove as much as possible of the precipitate from the paper into a weighed crucible, and ignite at low red heat. Burn the paper in a separate porcelain crucible and treat the residue first with a little nitric acid, which is afterwards evaporated off, and then with a drop or two of sulphuric acid. Ignite, weigh, and add this weight to the weight of the precipitate previously removed from the paper for amount of the lead sulphate.

In the above method an attempt was first made to precipitate the lead alone in a sulphuric acid solution without the addition of alcohol, but it was found that some of the lead sulphate was dissolved and low results were obtained. It was therefore thought best to add twice the volume of alcohol to the solution and acidify with sulphuric acid. A test was made to determine whether the arsenic in solution would be precipitated on the addition of this amount of alcohol, and the results showed it would not. The acid mixture of alcohol was used in washing the precipitate of lead sulphate free of arsenic for fear of precipitating this element by washing with 95 per cent alcohol alone. The 95 per cent alcohol was finally used for washing to eliminate the sulphuric acid.

Total arsenic oxid.—Transfer 100 cc of the nitric acid solution of the sample, prepared as in the above determination of lead, to a porcelain dish, add 6 cc of concentrated sulphuric acid, evaporate to a sirupy consistency on water bath and then on hot plate to the appearance of white fumes of sulphuric acid. Wash into a 100 cc flask with water, make up to mark, filter through dry filters, and use 50 cc aliquot for further work. Transfer this to an Erlenmeyer flask of 400 cc capacity, add 4 cc of concentrated sulphuric acid and 1 gram of potassium iodid, dilute to about 100 cc and boil until the volume is reduced to about 40 cc. Cool the solution under running water, dilute to about 300 cc, and exactly use up the iodin set free and still remaining in solution with a few drops of approximately tenth-normal sodium thiosulphate. Wash the mixture with a large beaker, make alkaline with sodium carbonate, and slightly acidify with dilute sulphuric acid; then make alkaline again with an excess of sodium bicarbonate. Titrate the solution with a twentieth-normal iodin solution to the appearance of a blue color, using starch as indicator.

The above method for arsenic oxid is a modification of the method of Gooch and Browning[a] and was applied to this class of goods both on account of its simplicity and because the same standard iodin solution used in determining arsenic in Paris green and London purple could also be used here. The original treatment with sulphuric acid is of course to eliminate lead. More sulphuric acid is added because it was found by Gooch and Browning that the potassium iodid acts best on the arsenic in sulphuric acid of a certain strength. The potassium iodid reduces the arsenic oxid to arsenious oxid and iodin is set free. This reaction is not complete unless the solution is boiled. The solution is boiled until its volume is reduced to about 40 cc. At this point nearly all the iodin has been volatilized, but a small amount is still present. This is used up exactly by dilute thiosulphate solution and the mixture is made alkaline so that the arsenic, which is now all in the form of arsenious oxid may be titrated with standard iodin to the form of arsenic oxid.

Water-soluble lead oxid.—Place 2 grams of the lead arsenate in a flask with 2,000 cc of carbon dioxid free water and let stand ten days, shaking eight times a day. Filter through a dry filter and use aliquots of this for determining soluble lead and arsenic oxids and soluble solids; determine lead as described above for total lead, using the same relative proportions of sulphuric acid, water, and alcohol, but keeping the volume as small as possible.

Water-soluble arsenic oxid.—For this determination use 200 to 400 cc of the water extract obtained under the determination of soluble lead oxid. Add 0.5 cc of sulphuric acid and evaporate it to a sirupy consistency, then heat on hot plate to appearance of white fumes. Add a very small amount of water and filter off lead through the very smallest filter paper, using as little wash water as possible. Place this filtrate in an Erlenmeyer flask, and determine arsenic as described above for total arsenic oxid, using the same amount of reagents and the same dilutions.

Soluble solids or impurities.—Evaporate 200 cc of the water extract obtained above to dryness in a weighed platinum dish, dry to constant weight at the temperature of the boiling water bath, and weigh. The soluble solids so obtained represent principally any sodium acetate or sodium nitrate present, with a very small quantity, perhaps, of lead acetate or nitrate and some soluble arsenic, probably in the form of lead arsenate.

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[a] Amer. J. Sci., 1890, *40:* 66.

Analytical Results.

To test these methods two samples of lead arsenate were prepared from lead acetate and sodium arsenate and two from lead nitrate and sodium arsenate. All the soluble salts were washed out, the samples in fact being made as chemically pure as possible. Since these soluble salts were removed a determination of soluble solids was useless. Following are the results obtained by two different workers, using entirely different standard solutions.

Results obtained on lead arsenate by the proposed methods.

Determinations.	Lead arsenate, chemically pure.					
	Prepared from lead acetate.			Prepared from lead nitrate.		
	Sample I.	Sample II.	Theory for lead arsenate.	Sample I.	Sample II.	Theory for lead acid arsenate.
Total arsenic oxid:						
Worker A	26.95	26.88	25.60	33.56	32.79	33.15
Worker B	26.24	26.17		32.90	32.92	
Total lead oxid:						
Worker A	72.11	71.80	74.40	64.13	63.86	64.26
Worker B	72.54	72.68		64.04	64.17	
Water of constitution (by difference):						
Worker A				2.31	3.35	2.59
Worker B				3.06	2.91	
Total:						
Worker A	99.06	98.68	100.00	100.00	100.00	100.00
Worker B	98.78	98.85		100.00	100.00	
Soluble arsenic:						
Worker A	.85	.70		.71	.63	
Worker B						

The table shows that the methods of analysis give very acceptable results. In the case of lead arsenate prepared from lead nitrate and sodium arsenate, it is evident that the compound lead acid arsenate ($PbHAsO_4$) is formed, and the results obtained on analysis are very close to the theoretical ones. In the case of lead arsenate prepared from lead acetate and sodium arsenate the results of the various determinations on lead and arsenic agree with each other quite well, but they are not so close to the theoretical results demanded for lead arsenate ($Pb_3(AsO_4)_2$) as might be desired, although they show that this compound is evidently formed to a large extent. Since there is a tendency on the part of both analysts to obtain slightly higher results on arsenic and slightly lower results on lead oxid, as well as slightly lower results on the total than is demanded by theory for lead arsenate, and since this tendency is not shown in the case of the other compound lead acid arsenate, it would appear that these variations are not due to inherent faults in the methods, but rather to the fact that some secondary reaction takes place, resulting in the formation of some compound other than lead arsenate. It is probable that this secondary compound is lead acid arsenate, since the presence of a small amount of it would account for the low result on lead, the high results on arsenic, and the low results on the total.

REPORT OF THE COMMITTEE ON FOOD STANDARDS, 1906.

Mr. President and Members of the Association: Permit me to present, on behalf of the committee on food standards, the following report of progress, covering the work of the year past. The committee has held during this period three meetings, namely, from November 20 to 21, 1905, at Boston, Mass.; from March 5 to 10 and June 18 to 25, 1906, at Washington. By means of circular letters and drafts of tentative proposals the members of the association have been informed from time to

time of the subjects upon whose consideration the committee was engaged. It may not be superfluous, however, to present at this time, for formal record in the proceedings of the association, a summary of the work performed.

The subjects announced for special consideration at the Boston meeting concerned more particularly the standards for fruits and fruit products, flavoring extracts, edible vegetable oils, and table and dairy salts; also the formulation of a description of suitable food containers, especially those made from tin plate, as necessarily involved, under the existing conditions of food transportation and preservation, in the conception of a standard food in respect of freedom from contamination by injurious substances.

At the hearings representatives of certain interests engaged in the manufacture of extracts urged the desirability of allowing some latitude in the use of synthetic flavoring materials, in standard preparations sold under names suggesting natural sources, the gist of the argument being that these synthetic products are chemically identical with the natural flavoring principles and cheaper than the latter. A number of valuable suggestions were made respecting the minimum strength of standard preparations and the importance of latitude in the choice of the process of manufacture by which the designated raw materials were to be converted into the finished product. In connection with fruit products, the use of glucose in the manufacture of preserved fruit, fruit butters, and jellies was discussed, and also the nomenclature of products into which glucose entered as a partial substitute for sugar as distinguished from those theoretically producible by the entire substitution of glucose for added sugar.

Several manufacturers of fruit products pressed the claims of evaporated apple cores and parings for admission as raw materials for the manufacture of standard apple products on the ground of the superior jelly-forming quality which the speakers attributed to them.

The subject of food containers was considered at several hearings, at which the inapplicability of the European standards to American conditions and difficulties was urged, and also the tendency to early deterioration of foods packed in lightly coated tin plate was discussed.

In addition to the subjects announced as the special topics for consideration at the Boston meeting, hearings were given to officers of the association of manufacturers of soda-fountain supplies, who presented their views respecting the standardization of fruit juices, fruit sirups, crushed fruit, and other flavoring materials used in the preparation of soda water. The ineffectiveness of simple sterilization for the preservation of these products and the need for intensification of color by use of foreign colors in these preparations were urged.

The processes employed in the manufacture of rum were presented by Dr. H. Sawyer, and the rum standard was discussed in the light of these processes and the existing analyses of rum. The representatives of other liquor interests presented their views as to the nature of whisky and of the various so-called "blended" spirituous liquors now sold to American consumers.

Representatives of large meat packing interests urged that the meat standards already proclaimed be so amended as to specify saltpeter among the admissible constituents; also, that the standard for salt include a water maximum, owing to the great variability in the amounts of this constituent exhibited by salts shipped in bulk to consumers buying in large quantities.

In executive session, the committee reviewed the correspondence received upon the subjects assigned for action and spent some time in amending the tentative schedules for flavoring extracts, edible vegetable oils, and fruits and fruit products, providing for further correspondence on certain points. Preliminary drafts of schedules for ice cream and for spirituous liquors were also prepared.

The committee assembled in March of this year to complete its work on the standards above mentioned as the special topics of consideration at the Boston meeting. The sessions were chiefly executive, no hearings being given, though much time was given to consultation with experts in the Department of Agriculture upon important points. The representatives of certain trade interests having noted the occasional presence of borax in refined salt, F. W. Woll, referee on salt, and W. D. Bigelow had been requested to investigate the matter. The reports from their investigations upon samples representing the chief regions of production indicated that the turmeric tests for borax, ordinarily used in the detection of the substance as a food adulterant, are not sufficiently delicate to reveal the traces occasionally present in refined salt. Messrs. Bigelow and Chace presented data bearing upon the limits for sugar in fruit preserves, jams, etc.; Mr. Tolman, data respecting the range of variation exhibited by the physical properties and chemical constituents of edible vegetable oils; Mr. Gore contributed data upon the distribution of the pectins in various parts of the apple, having a bearing upon the claims made for the cores and parings as sources of jelly; Mr. Kebler made a number of valuable suggestions relative to the standards for essential oils and for the flavoring extracts prepared therefrom; Mr. Webster, chief of the dairy division, Bureau of Animal Industry, reported upon the present status of the term "factory-filled" as applied to refined salt. Mr. Coville, botanist of the Department of Agriculture, revised the scientific botanical terms used in the standards, to insure their conformity to the principles of botanical nomenclature now in vogue.

At this session the committee determined upon recommendations for standards belonging to the schedules for fruit and fruit products, flavoring extracts, edible vegetable oils, and salt. These recommendations were approved by the honorable the Secretary of Agriculture, and were proclaimed by him on March 8, 1906, as the National standards established for the respective foods under the authority granted by act of Congress. Since these standards have been published, as Circular No. 17, Office of the Secretary, U. S. Department of Agriculture, and distributed to the members of the association, no detailed comment upon them will be made in this report. It may be noted, however, that in connection with the schedule for flavoring extracts, the desirability was considered of fixing the standards upon the formulas of the United States Pharmacopœia for all the flavoring preparations described in that publication. It was finally decided, that while the formulas there given afford the best basis for the standards for certain flavoring preparations, in many cases the formulas have evidently been prepared with reference to the use of the product for flavoring medicines rather than foods. Each extract was therefore considered independently, and the minimum of strength fixed in accordance with the best information obtainable. Furthermore, inasmuch as the 1900 Revision Committee of the United States Pharmacopœia had declared that the pharmacopœial directions for making drug preparations were not intended to serve as standards for preparations made for non-medicinal uses, it was deemed best to accompany the standards recommended by the committee for flavoring extracts, with the complementary declaration that the flavoring extracts described are intended solely for food purposes and are not to be confounded with similar preparations described in the Pharmacopœia for medicinal purposes.

At the March session tentative drafts of schedules for ice cream, vegetables and vegetable products, tea and coffee, prepared mustard, and malt liquors were formulated for submission to the members of this association and to the trades concerned, for criticism and suggestion; a revised draft of a description of suitable containers for holding preserved foods was also included. The subject of standards for spirituous liquors was given considerable study in the light of existing analyses and manufacturing processes.

Finally, for the purpose of organizing the work upon cattle food standards, which had been committed by the association at the 1905 meeting to this committee, it was ordered that certain members of the association be requested to collaborate with the

committee, as referees on particular groups of cattle foods, and to present tentative standards for the corresponding products.

To guide the referees, it was ordered that the standards to be proposed should—

(*a*) Be minumum standards, similar in purpose to those already proclaimed for human food.

(*b*) Conform in form of expression to those for human food.

(*c*) Be based upon data representing American products; that is, that they should be based upon a careful study of American raw materials, manufacturing methods, and nomenclature of manufactured products.

It was also decided that—

(*d*) Before the adoption of any schedule of standards, the trade be fully consulted.

(*e*) So far as they apply, the standards already adopted for grains and grain products in the schedules for human food be adopted for the corresponding cattle foods.

Considerable difficulty has been experienced by the writer in enlisting the aid desired, owing to the tremendous pressure upon the time and energies of our experiment station workers. The list of referees, so far as completed, is as follows:

Committee on buckwheat, millet, sorghum, dhurra, their products: Mr. John P. Street, of New Jersey; Mr. Frank Fuller, of Pennsylvania; Mr. L. H. Merrill, of Maine.

Committee on wheat, rye, oats and spelt, and their products: Mr. Harry Snyder, of Minnesota; Mr. Charles H. Jones, of Vermont.

Committee on corn and its products: Mr. M. A. Scovell, Kentucky; Mr. H. C. Midsall, Iowa; Mr. J. B. Lindsey, Massachusetts.

Committee on linseed products and other oil cakes and oil meals, except cotton-seed meal and maize corn: Mr. H. A. Weber, of Ohio; Mr. E. F. Ladd, of North Dakota.

Committee on cotton seed and rice products: Mr. B. B. Ross, of Alabama; Mr. B. W. Kilgore, of North Carolina; Mr. G. S. Fraps, of Texas.

Committee on barley and brewer's and distiller's grains: Mr. F. W. Woll, of Wisconsin.

Committee on beet pulp and other wastes from sugar manufacture, molasses grains, also leguminous seeds and seed products used for cattle foods: Mr. J. E. Halligan, of Louisiana.

During the interval between the March and June meetings, the tentative schedules for ice creams, vegetables and vegetable products, prepared mustard, cocoa butter, tea and coffee, and malt liquors were distributed for criticism to the members of the association and to the several trade interests concerned; also, the tentative description of suitable vessels for holding preserved food products was sent to a list of the principal manufacturers of tin plate and tinware, prepared for the use of the committee through the courtesy of the Secretary of Commerce and Labor.

At the June meeting the correspondence respecting the tentative schedules above mentioned was carefully reviewed. Hearings were given to a number of interests. Upon the subject of food containers representatives of the tin-plate manufacturers, of the American Tin Can Company, and of vegetable packers discussed the question of standard containers from their respective points of view. The committee finally decided to extend the description so as to include the metallic foils used in wrapping food products, to designate the quality of tin plate suitable for making containers for certain classes of foods known to corrode defective plate, and to make certain specifications for the lacquered cans now coming rapidly into use as containers for colored fruits and vegetables, such as strawberries and beets.

Mr. Sawyer requested a somewhat broader standard for rum than he had earlier recommended, in view of certain experiments now in progress at the distillery where he is engaged.

A representative of the makers and importers of the terpeneless oils of lemon and orange urged a widening of the standards for the terpeneless extracts of lemon and orange, to permit the use of these oils in the preparation of the corresponding extracts. This change was later made.

Representatives of the wine industry in the eastern United States urged a revision of the standards for wine and sugar wine, so that the use of a limited amount of sugar

or sugar sirup with the must might be included as a legitimate cellar treatment for wine, the low saccharine content of the must of the grapes of this region making it difficult to manufacture a satisfactory wine without the use of sugar, and the manufacturers objecting to the name "sugar wine" as suggestive of an extreme use of sugar for such wines. In view of the conditions of the wine trade in America, especially as they appeal to the consumer, it was decided that the broadening of the standard for wine would not be wise; but to relieve the makers of the possible implication attaching to the term "sugar wine," the term "modified wine" was adopted as a designation for wines in preparing which a limited quantity of sugar or sugar sirup has been used.

A communication was received from the Italian ministry of agriculture, Chevalier Rossati urging that the maximum limit for volatile acids in wine be raised, since the limits in the standard established exclude an important group of Italian wines of good quality. It was found, however, that our official method for determining this constituent gives lower results than the method usually adopted in Italy, and hence, that the anticipated difficulty in the entry of wine of good quality would probably not occur with frequency.

Representatives of the manufacturers of vegetable products, especially canned corn and catsup, discussed the use of sugar and saccharine in the former and benzoate of soda in the latter product, and Mr. Alexander Leckey, of London, England, urged a more liberal standard for cocoa prepared by the so-called "Dutch process," and the permission to import and sell this cocoa preparation under the name "soluble cocoa."

Finally, a committee from the United States Brewers' Association urged certain modifications of the proposed standards for malt liquors. Especial objection was made to the establishing of a separate standard for malt beer, to the specification of a minimum storage period for lager beer, and to the exclusion of brewers' sugars from the raw material used in the brewing of ale, porter, and stout. The manager of the Corn Products Company urged, in addition, that "refined grits," a corn-starch product, should be named, as well as unmalted cereals, in the list of raw materials for the preparation of beer.

The tentative schedules published in May were then reviewed in the light of the various criticisms received, were somewhat amended, and finally recommended for proclamation by the Secretary of Agriculture.

Much of the time at the sessions of this meeting was spent in a revision of the standards earlier proclaimed, as the drift of legislative action in April and May made it uncertain whether the authorization given the Secretary of Agriculture to fix standards would be continued after June 30, 1906. It was therefore deemed important that such amendments as seemed desirable in view of information gained since the publication of the several standards be made while the power to amend unquestionably remained.

A number of minor changes were accordingly made in the standards earlier published. The revised schedules were issued as Circular 19 of the Office of the Secretary, superseding and supplemental to those published in Circulars Nos. 13 and 17. As the revised standards have been sent to the members of the association, no extended statement concerning the amendments is necessary in this report. Your attention is, however, briefly called to the insertion of a standard for cold-storage meat, as distinct from fresh meat; to an extension of the limit for the colostral period in the milk standard; a modification of the fat standards for condensed milks; a change in the cheese standards to bring them more closely into conformity with the definitions in the act of June 6,1896; the raising of the water maximum for oatmeal; dropping the standard for so-called whole-wheat flour, because the name is misleading; the adoption of a general definition for fruits; the specification of limits of composition for maple sugar and sirup on the basis of investigations made and data compiled by the Bureau of Chemistry for the

use of the committee; the dropping of the standards for corn and glucose sirups, earlier recommended to conform to the legal definitions of a few States, the standards being dropped because they did not fully conform to the principles of standardization adopted by the committee; the modification of the standard for candy, to bring it into conformity with the definition in the food and drugs act; the insertion of a standard for cottonseed oil stearin, and the change of the limits of acidity for wine vinegar and of solids for malt vinegar, in the light of more comprehensive data at the command of the committee.

It was considered desirable to give further consideration to the schedule for malt liquors, so that action upon these standards was postponed.

It should be noted in relation to the meetings of March and June, that the committee was favored by the collaboration of Mr. Elton Fulmer at the former meeting and Mr. Richard Fischer at the latter, these gentlemen having been especially commissioned as experts by the Secretary of Agriculture, so that the National Association of State Dairy and Food Departments, whose cordial cooperation is important in securing the unification of State standards, might be brought more closely into touch with the current work of this committee. These collaborators joined in each instance in the recommendations made to the Secretary of Agriculture.

It is not possible at this time to present to you the current work on cattle-food standards, but the work is steadily progressing, recommendations having been received from the referees on buckwheat and maize products, animal products, sugar-beet pulp, and molasses grains, and other recommendations are promised for the near future. It is our hope that the committee may begin its part of the work of comparing and unifying these standards at a meeting to be held during the coming month.

In closing, I desire to voice the appreciation of the committee for the cordial interest and cooperation of the members of the association, and especially for the steady support and valuable counsel of the honorable the Secretary of Agriculture, with whom the committee has been called to collaborate.

On behalf of the committee.

William Frear, *Chairman.*

On motion the report of the committee was accepted and the committee continued.

Mr. Wiley. I wish to emphasize the importance of the cooperation now existing between the food standards committee of this association and that of the National Association of State Dairy and Food Officials, the latter committee including Messrs. Jenkins, Scovell, Fischer, Barnard, and Fulmer. These committees now meet as one under the authority of the act authorizing the Secretary of Agriculture to collaborate "with the Association of Official Agricultural Chemists and such other experts as he may deem necessary to ascertain the purity of food products." While some degree of cooperation has existed in the past the complete union of these two committees can not but be extremely beneficial to the work both in the formulation of the standards and in securing the adoption of the standards agreed upon in States where no legislation exists to the contrary, thus bringing the State and Federal regulations into harmony.

REPORT OF THE COMMITTEE ON FERTILIZER LEGISLATION.

By H. W. Wiley, *Chairman.*

During the past year the chairman has had little opportunity either to study the subject of a National fertilizer law or to communicate on the subject with his fellow members. He has, however, acting under the instructions of the committee, had two conferences with Mr. W. H. Bowker, representing the manufacturing interests. It was the opinion of the committee that any legislation which might be framed should, if possible, receive the support not only of the State chemists charged with the inspection of fertilizer materials, but also of the agricultural manufacturing interests. It is believed by your committee that it is possible to frame a measure so ethical in its principles and so general in its application as to merit and secure the support of all interested parties. To this end the chairman submitted to Mr. Bowker a rough draft of a proposed measure drawn for the purpose of regulating interstate commerce in fertilizing materials, and asked him also to submit a tentative measure which the committee might consider. In answer to this request a reply was received from Mr. Bowker under date of October 18, 1906, which read in part as follows:

You will remember that you asked me in the spring to prepare a tentative bill acceptable, in my opinion, to the fertilizer interests, and I have been working on such a measure, but it does not altogether suit me, and, what is more to the point, I could not offer it as a measure which, in my opinion, would be acceptable at this time, to the fertilizer manufacturers. I am afraid that there are as many minds as there are manufacturers, and that we can never get together until we are face to face with proposed legislation. When I last saw you in New York you will remember that you expressed the opinion that the matter should go over for a year or two, and I concurred. In that event you and your associates can study the matter and come to some agreement, and meantime I will see what can be done with the manufacturers.

Anything which I might present now would be only my personal measure, and * * * I am not willing to stand sponsor for any measure without further consultation. I think, therefore, the whole subject should be left as it was last fall, and you will recall that I suggested in my remarks that the official chemists should first get together and agree upon some measure and then submit it to the manufacturers, who, when they are face to face with such a proposition, will, no doubt, appoint a committee to meet a committee of your association. * * * I think it would be premature for me to present a measure now and perhaps create discord, whereas, in the interests of the whole, we want harmony and cooperation. * * *

After a conference with Mr. Bowker the chairman addressed the following letter to him on October 29, 1906:

I am very content to let the matter rest awhile until there is more of a crystallization of sentiment regarding it. I think in the end there should be no difficulty in an agreement between our association and the association of manufacturers. I think this for two reasons; first, the association of manufacturers is made up of honest men, who want to give the equivalent of the prices for the goods which they furnish. They are men who are perfectly willing to mark their goods so as to show their character. On the other hand, our association is composed of honorable men who wish to secure the protection above mentioned for their clients and for the farmers. There are many details respecting the character of labeling and the character of the guarantee, the discussion of which should be approached in a friendly spirit. * * *

During the past year, as you all know, important measures regulating interstate commerce in foods and drugs were pending before the Congress of the United States. To secure successful legislation on these measures required the united efforts of all interested parties. It appeared to your committee that it would be unwise at such a time to distract the attention of Congress and of the friends of legislation by asking for the consideration of another measure of a similar character. If the principle of the control of interstate commerce in products of this kind is successfully maintained in the administration of the food law and is supported by the courts, it will be less difficult in the future to secure the needed legislation of a National character affecting interstate commerce in fertilizers.

It is considered to be the duty of this committee to call attention also to the reasons which occur to many for considering the proposed legislation inopportune or unnecessary. One of the chief of these reasons is the fear that National legislation regulating interstate commerce in fertilizers may interfere with existing State legislation, especially in regard to fees for inspection or licenses. These views were well summarized in the National Stockman and Farmer for November 8, 1906, from which the following excerpt is taken:

We do not favor any such legislation at this time for several reasons, a few of which will be mentioned. First, there is no necessity for a National fertilizer law and no demand for it by the people in whose interest such legislation should be enacted. There is no necessity for it, because twenty-seven States have fertilizer laws of their own—every State in which fertilizers are used in any quantity. These laws are enforced by State officials, with the aid of the experiment stations in some cases. As a rule they are adapted to the needs of the States and are as well enforced as other State laws—better perhaps than a National law could be enforced. That they are satisfactory to the interests they are intended to protect is evident from the lack of complaint by those interests, who are responsible for their existence. If there is any demand from farmers for a National fertilizer law, we have never heard of it. No agricultural or live-stock association, no agricultural journal, that we know of, has voiced such a demand. The chemists and the manufacturers of fertilizers seem to be the sole power behind the movement, and they are not the people in whose interest fertilizer legislation should be brought forward.

It is therefore recommended that the committee be continued, but with instructions to secure, if possible, the collaboration of the great fertilizing interests in the perfection of a measure which in the future may be submitted to the Congress of the United States with the joint approval of the manufacturing interests and the Association of Official Agricultural Chemists.

H. W. Wiley, *Chairman.*
H. B. McDonnell.
B. B. Ross.

On motion by Mr. Frear the report was ordered to be received by the association, and the committee continued.

Mr. McCandless. The Georgia fertilizer law is the one agreed upon at the Hot Springs convention in 1900 by the Cotton Association of Commissioners of Agriculture and the fertilizer manufacturers. A bill was drafted by the commissioners, with the advice of the State chemists, and was discussed for several days, section by section, with the result that a measure acceptable both to the manufacturers and the commissioners was finally adopted.[a] This measure was immediately enacted into a law in Georgia. Alabama and Tennessee followed our example, and, I believe, Mississippi. We have been operating under this law ever since, and I believe we have in it a nucleus for a National fertilizer law which would be acceptable not only to the State officials, but also to the great manufacturing interests.

Mr. Frear. It occurs to me that there is one class of interests which has not yet been brought into touch with this movement whose judgment and collaboration it is desirable to have. I refer to the officials charged with the execution of the State fertilizer laws. Some of us are simply chemists whose duties end with the examina-

[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 81, p. 207.

tion of the samples and an expression of opinion as to their quality. All the other duties of the fertilizer control are conducted by officials of superior rank. A certain uniformity in the requirements as to labeling, declaration of materials, and the return that should be made for the money expended is highly important, and the method of securing such uniformity ought to be considered by all concerned. I should like to see the scope of the committee enlarged, so as to bring into consultation these State officials.

Mr. Wiley. As the fertilizer control is almost exclusively in the hands of the agricultural experiment stations, which this association primarily represents, I think the committee would naturally consult the other officers connected with the fertilizer control without further instructions.

Mr. Bowker. As a manufacturer I wish to say that while we are not seeking this law, as the report of the committee might seem to imply, but are satisfied to work under the present State laws, still if it is decided that a National law will be better we will accept that decision, provided the law is one under which we can work. I do think that some uniform statement of analysis is very desirable; whether a National law shall go any further than that is for the various interests to determine. We have no wish to avoid paying license fees under a National law, but in some States there are no fees, and it does seem as though there should be some uniformity in the matter. For example, it seems to me unjust that the State of Rhode Island should charge $18 for a complete analysis when we only pay $15 in some of the States that use many times as much fertilizer.

It seems also that there should be some change in the statement required in regard to certain fertilizer ingredients, particularly potash. If it is proper to give the water-soluble and available phosphoric acid, why not give the water-soluble and available potash? The reverted phosphoric acid is determined by a purely arbitrary method, and a similar arbitrary method could be adopted for the determination of available potash. In all of the organic substances used in fertilizers, and there are many of them, there is from 0.25 to 3 per cent of potash, for which the manufacturer gets little if any credit under the present method. In closing, let me say again that the manufacturers do not oppose the State laws and they will not, in my opinion, oppose a National law, provided it is fair to all interests.

Mr. McCandless. We have found in Georgia during the past season considerable adulteration of the nitrogenous materials mixed with commercial fertilizers, and I should like to present a short paper on the subject, if it is the pleasure of the association.

ADULTERATION OF COMMERCIAL FERTILIZERS.

By J. M. McCandless, *State Chemist, Georgia.*

In the past few years the price of nitrogen has been rising by leaps and bounds, and of course the temptation to use any substitute has grown continually. In the summer of 1905 we became suspicious that all was not right with Georgia fertilizers, and our department sent out a circular letter to the fertilizer trade, warning them against such materials as dried muck or peat and materials containing cyanogen compounds, samples of which had fortunately been obtained. At the beginning of the season of 1905–6 a systematic examination was begun of every sample to determine the nature of the ammoniating material. It was not long before leather and also Prussian blue or ferrocyanid of iron were discovered in the samples of mixed fertilizers. Our law prohibits the use of leather in fertilizers, unless it is registered at the department of agriculture as a source of ammonia and satisfactory evidence submitted to show that it has been so treated as to render it available. In the cases referred to no such registration or evidence had been submitted, but the samples on analysis by the pepsin-hydrochloric acid method, and by the alkaline permanganate method, showed an availability of about 75 per cent, so that the violation of the law was technical rather than real, especially as the goods were sold to manufacturers under the name of tankage, and the only action taken was to seize a car belonging to a maker of the treated leather and ship it out of the State, at the same time publishing the fact.

In the case of the samples containing Prussian blue or ferrocyanid of iron the available nitrogen was low, as was to be expected, and the names of the manufacturers have been published in our annual bulletin. This Prussian blue has been put on the market under the names of beet-root manure, potash manure, and fillerine. An examination of these raw materials showed them to be composed chiefly of oxid of iron, ferrocyanid of iron, free sulphur, ammonium-sulphocyanid, ammonium sulphate, and naphthalin, evidently showing them to be of gas-house origin. Although sulphocyanids can readily be detected in the original material, after mixing with acid phosphate, the reaction seems to be prevented by the presence of phosphoric acid, so that sulphocyanids can not be detected in the mixed goods by the iron test. The Prussian blue, however, can readily be detected.

Other materials of a low nitrogen availability that are found on the market are dried muck or peat, mora meal, and grape or tartar pomace. The systematic plan of procedure for the detection of adulterants which was adopted last season is as follows:

Prepare a dilute solution of sulphuric acid (25 cc of concentrated acid to 1 liter of water), also a dilute solution of caustic soda made by adding 100 cc of sodium hydroxid solution of 1.40 sp. gr. to 1 liter of water. In the examination for organic adulterants, as leather, muck, mora meal, place 5 to 10 grams in a porcelain dish, stir with water, and then agitate in the same way that a gold miner treats the pulverized ore in his pan, bringing the lighter organic matters to the surface and transferring them to a small beaker, in which they are washed two or three times by decantation to remove as much soluble phosphoric acid as possible. Then pour 10 or 15 cc of the dilute sulphuric acid onto the residue and bring the whole to a boil, remove the lamp and smell the hot solution at once. In the presence of leather its unmistakable odor will be noted in almost every case; filter the solution and test for tannic acid by Dabney's test.

Usually the simple neutralization of the sulphuric solution with ammonia is sufficient to give the purple-wine color characteristic of leather. Further confirmation of the presence of leather is obtained by transferring the residue on the filter to a small beaker and boiling with the dilute solution of caustic soda; if leather be present it

dissolves completely, producing a deep red color. Some experiments were made which show that an approximate determination of the percentage of leather present may be made by comparing the color of the diluted solution with that of a standard solution of leather dissolved at the same time and under the same conditions. If leather be absent and muck present, no reaction takes place until treatment with the dilute boiling caustic soda solution, when in the presence of muck a deep brown-black solution will be obtained. Mora meal gives a strong reaction for tannic acid and might be easily mistaken for leather, as it also gives a deep red color on treatment with caustic soda solution. But it differs from leather in yielding a different odor on boiling with dilute sulphuric acid and in not dissolving in the caustic soda solution completely. On boiling a small portion of leather with soda twice, decanting, and washing no further color will be obtained from the leather, but if mora meal be present, the hot soda extracts a red color for three or more treatments. Under the microscope also mora meal differs from leather.

The heavy residue from the panning to remove organic matter will contain the Prussian blue and it may be detected by boiling with dilute caustic soda, filtering, neutralizing with hydrochloric acid, and adding a drop or two of ferric chlorid, when a blue color or a precipitate of Prussian blue will be obtained. If considerable organic matter be present and the Prussian blue has been used only in small quantity, a green solution will develop on standing a few minutes, due to the fact that the yellow color derived from the organic matter gives a green with the blue derived from the ferrocyanid.

It is not inappropriate to call attention to the fact that we shall afford a much more perfect protection to the consumers of commercial fertilizers by hunting for specific low-grade materials in mixed fertilizers than by attempting to determine the availability of the nitrogen in any given sample. For instance, suppose a mixed fertilizer to contain in one ton 600 pounds of an ammoniating material showing an availability of 95 per cent and 200 pounds of a worthless stuff showing an availability of only 30 per cent. The mixed goods would show an availability of 78.7 per cent and be rated very high.

REPORT OF THE COMMITTEE ON DEFINITION OF PLANT FOOD.

Attention is called to the report of last year, published on page 197 of Bulletin 99 of the Bureau of Chemistry. Your committee has considered the basic principles of the definitions proposed by the committee of which Professor Barnes was the chairman and our own, and are of the opinion that the language of a definition which would be agreeable to all parties has not yet been invented. Your committee is further of the opinion that the difference between the two apparently opposing schools is more a matter of verbiage than of reality. The committee of the botanists defines what your committee reports as "plant food" as "food materials." It appears that this is rather a distinction than a difference, Nevertheless, it has appeared advisable to secure additional information on this subject, and to this end your committee has consulted some of the leading authorities and has made liberal extracts therefrom. The following authorities have been examined:

(1) A Manual of Botany, by J. Reynolds Green, 1902, Vol. II, Classification and Physiology. Green unequivocally and tersely supports the Barnes theory respecting plant foods. This is especially brought out on page 405 of the book.

(2) Food and the Principles of Dietetics, by Robert Hutchison, Assistant to the London Hospital, third edition, 1901. Hutchison defines food as follows: "A food may be defined as anything which, when taken into the body, is capable either of repairing its waste or furnishing it with material to produce heat for nervous or muscular work."

(3) Standard Dictionary: "Food is that which is eaten or drunk for nourishment; aliment; nutriment, in a scientific sense; any substance that, being taken into the body of animal or plant, serves, through organic action, to build up normal structure or supply the waste of tissue; nutriment; aliment, as distinguished from condiment.

"Plant food—anything adapted to sustain the growth of plants; the portion of natural materials or of fertilizers that plants can assimilate."

(4) Webster's Dictionary: "Food is what is fed upon; that which goes to support life by being received within, and assimilated by, the organism of an animal or a plant; nutriment; aliment; especially, what is eaten by animals for nourishment."

(5) Century Dictionary: "Food is what is eaten for nourishment; whatever supplies nourishment to organic bodies; nutriment; aliment; victuals; provisions. 2. Anything that sustains, nourishes, and augments. 3. Anything serving as material for consumption or use."

(6) A Digest of Metabolism Experiments, by W. O. Atwater and C. F. Langworthy, Bulletin 45, Office of Experiment Stations, 1898. These authorities also define food as that which is taken into the body.

(7) Farmers' Bulletin 142, U. S. Department of Agriculture, Principles of Nutrition, by W. O. Atwater, 1902. This also supports the theory that foods are only the materials entering the body. He says, "Food is that which taken into the body builds tissues or yields energy."

(8) Manual of Cattle Feeding, by Henry P. Armsby, fifth edition, 1890. Armsby also sustains the theory that the term foods is applied to substances entering the plant or animal body.

(9) The Principles of Animal Nutrition, by Henry P. Armsby, 1903. This work also sustains the theory above mentioned.

(10) Feeds and Feeding, by W. A. Henry, sixth edition, 1904, page 3. "How plants gather food." Henry shows that the inorganic materials entering the plant are the real food thereof.

(11) Lectures on the Physiology of Plants, by Julius von Sachs, edition of 1887, page 282. Sachs strongly supports the theory that the food of plants is what enters them from without.

(12) Agricultural Botany, Theoretical and Practical, by John Percival, second edition, 1902, page 201. Percival rather takes both sides of the case, saying, "Green plants likewise need food of a similar complex nature for development and growth; they are, however, not generally adapted to obtain compounds of this character from their surroundings, but are able to manufacture them from inorganic compounds, such as carbon dioxide, etc."

(13) Works of Liebig. Liebig was perhaps the original founder of the inorganic theory of plant foods, and supports it strongly throughout all his works.

(14) The Relations of Plants to the Soil, by J. A. Cl. Roux, Paris, 1900, page 3. Definition of Plant Food.—"Every body which penetrates into the plant and which alone or combined with other bodies helps in its nutrition constitutes a food. The foods are gaseous (oxygen, carbonic acid, nitrogen); liquid (waters); and solid (organic and mineral matters)."

(15) A Text-Book of Plant Physiology, by George James Peirce, 1903, page 43. Peirce supports the theory that food is what is taken into the body.

(16) Lectures on the Physiology of Plants, by Sydney Howard Vines, edition of 1886, Lecture VIII, page 122. Vines strongly supports the theory which considers foods as the substances which enter the organism.

(17) Die Landwirthschaftlichen Versuchs-Stationen, vol. 29, 1883, page 253. Article by von Raumer recognizes mineral matters as foods of plants. Same work, 1878, page 100, vol. 21—a distinct recognition by Stutzer of the mineral food of plants.

(18) The Physiology of Plants, by Wilhelm Pfeffer, vol. 1, second edition, Ewart's translation. Recognizes the external origin of foods for plants.

(19) Lectures of Jost, 1904. In the seventh lecture, page 95, he sets forth the principle of the inorganic character of the food of plants.

(20) How Crops Grow, Johnson, edition of 1900, pages 366–369. A strong support of the mineral food theory of plants.

(21) The Nutrition of the Plant, by Louis Grandeau, Paris, 1879, page 3. A strong support of the mineral theory of plant food.

(22) Annales de la Science Agronomique, second series, third year, 1897, vol. 1, page 175. Gives strong support to the mineral theory of plant food.

(23) The Physiological Rôle of Mineral Nutrients in Plants, by Dr. Oscar Loew, Bulletin 45, Bureau of Plant Industry. Preface by Dr. Albert F. Woods, supporting the theory of the mineral nutrition of plants.

(24) Agriculture in Some of Its Relations with Chemistry, by F. H. Storer, seventh edition, vol. 1, 1897. He says, "On considering the relations in which plants stand to the air and the soil which surround them, the questions naturally arise, What are the sources from which plants derive food? and, How is it that plants take in their food?"

(25) How Crops Feed, by Samuel W. Johnson, edition of 1900. Complete recognition of the theory of mineral plant food.

(26) Annales de la Science Agronomique, second series, 1902–3, vol. 1. Complete exposition of the mineral theory of plant nutrition.

(27) A Text-Book of Botany, by Edward Strasburger, Fritz Noll, H. Schenck, and A. F. W. Schimper, 1903, page 171. "The Essential Constituents of Plant Food." Complete exposition of the mineral theory of plant food.

Many more authorities might have been secured, but, as will be seen, fully half of those consulted are botanists, and all but two of the authorities consulted give unequivocal support to the theory that plant foods are wholly of external origin and principally of a mineral character. It does not seem wise to prolong a discussion which turns simply upon the meaning of a phrase. It is perfectly evident that our botanical brethren who differ from us in our definitions do so only pro forma. We can not see what difference there is between the expressions "foods" and "food materials." They mean one and the same thing. Your committee therefore recommends that we adhere to our definition of plant foods as those substances entering the plant from without and which are utilized in the metabolic activities, and that we adopt the definition of our botanical brethren as food materials meaning the same thing to them as foods do to us.

Respectfully submitted.

H. W. Wiley, *Chairman.*
L. L. Van Slyke.
E. W. Magruder.

The report was accepted by the association and the committee discontinued

The meeting adjourned.

FRIDAY—AFTERNOON SESSION.

REPORT OF THE COMMITTEE ON THE TESTING OF CHEMICAL REAGENTS.

By L. F. Kebler, *Chairman.*

Since the last annual meeting of the Association little work of note has been done in testing chemical reagents. The committee of the American Chemical Society in charge of this subject met last March and discussed ways and means for the purpose of placing the nomenclature on a satisfactory basis and the tentative names agreed upon were to be submitted to various manufacturers, not only in this country, but also to foreign manufacturers, for criticism and suggestions. The impurities to be considered in connection with a number of chemicals were also discussed.

The secretary of the committee has informed the writer that as yet very few definite replies have been received from the manufacturers consulted. Particularly was this true of the foreign manufacturers. In view of the fact that during the two previous years little had been accomplished by laboratory work, it was decided to pursue another course. The work was confined to testing the various chemicals commonly employed in analytical work for the presence of arsenical compounds and chlorids.

The Occurrence of Arsenic in Chemical Reagents.[a]

The first point to be considered in undertaking this work is to ascertain what method or methods are most suitable. Among the methods tried may be mentioned, first, the Gutzeit test, which is based upon the reaction of arsenureted hydrogen and mercuric chlorid. The test is usually made by placing the acidified solution of the sample in a test tube containing metallic zinc and allowing the generated gas to pass through a plug of cotton or asbestos containing purifying and drying agents, and then to diffuse through a mercuric chlorid spotted filter paper placed over the mouth of the test tube. Many modifications of this method have been proposed, but no general agreement as to its value has apparently been reached. From our own experiments the conclusion is drawn that this method is unreliable for quantities of arsenic less than about ten parts per million.

The second method to be mentioned is that known as the Reinsch test and depends for its applicability upon the deposition of arsenic from a warm hydrochloric-acid solution upon the surface of pure copper foil in contact with the liquid. The arsenic so deposited can then be removed from the copper foil by heating in a hard glass tube. The arsenic is oxidized to arsenious oxid and condensed as a white sublimate in the colder part of the tube. This method has not given satisfactory results in this investigation.

The Marsh-Berzelius method was carefully tested and found to give the most satisfactory and reliable results. The only objection to the method is the amount of time necessary to operate it. Many modifications have been suggested, but the principle of all is the same and the degree of accuracy which can be obtained is probably due more to the care exercised by the individual worker than to the new and improved forms of apparatus which may be used.

In the work described in this paper the ordinary Marsh-Berzelius apparatus and the electrolytical apparatus of the form described by Thorpe [b] were used indiscriminately throughout. No novel features were introduced in the case of either apparatus and it therefore does not appear necessary to describe in detail the general procedures. A number of experiments indicated that the arsenic mirror obtained by the electro-

[a] The experimental part of the work was done by A. Seidell, Bureau of Chemistry.

[b] J. Chem. Soc., 1903, *83:* 974.

lytical and Marsh-Berzelius methods are comparable in all respects and therefore that equally satisfactory determinations can be made by using the one or the other apparatus.

The chemical reagents tested in this work are purchased on annual contracts awarded to different firms. It therefore happens that the chemicals reported represent only a few manufacturers. From our general experience, however, they are fairly representative of the quality of chemicals usually supplied to chemists. It will be seen that while many of the samples contained practically no arsenic, there are a few others in which its occurrence appears general. Only five of the twenty-three samples of ammonia salts, including the acetate, carbonate, chlorid, nitrate, etc., were found to contain appreciable quantities of this impurity. Two samples of ammonia alum contained, respectively, 37.5 and 40 parts of arsenic per million. From this it appears that with the possible exception of ammonia alum the occurrence of arsenic in ammonia salts is uncommon, and when found its presence is probably due to accident rather than to any inherent tendency of the product to retain arsenical compounds.

Out of seven samples of barium salts, two showed 1 part per million of arsenic each.

Six samples of boric acid were examined, and one marked "U. S. P." was found to contain 10 parts per million of arsenic. The others were free from this impurity.

The calcium salts examined consisted of three samples of carbonate, six of the chlorid, twelve of the oxid, and two of sulphate. Of these, arsenic was found in one of the carbonate samples, three of the chlorid, and in both of the sulphate samples. From this it appears that calcium salts are more or less contaminated with arsenic and therefore should be carefully tested when the subject of arsenic investigations are under consideration.

Three out of six samples of copper sulphate contained fairly large amounts of arsenic.

It has been known for a number of years that glycerin is particularly apt to contain larger or smaller quantities of arsenic. During recent years, however, the amounts present in this chemical have been materially reduced; but that glycerin is not free from this impurity is attested by the analyses made public from time to time. In confirmation of these reports we find that of fifteen samples received from nine different sources all except one showed distinctly measureable amounts of arsenic. The amount found varied from a trace to 3 parts per million.

Only one of six samples of sulphuric acid showed a faint trace of arsenic. On the other hand only one sample out of six of hydrochloric acid was free from this impurity although it is frequently sold as being arsenic free. All of the samples of nitric acid examined indicated the presence of traces of arsenic.

The potassium salts are comparatively free from arsenic compounds. Out of twenty-four samples examined only the permanganate and sulphite indicated the presence of considerable quantities of arsenic. The permanganate samples were secured from three different manufacturers and contained from 3 to 7 parts per million. One sample of potassium sulphite was found to contain 70 parts per million of arsenic.

Thirty-six samples of sodium salts were examined. Of these all were fairly free from this impurity, except the sodium sulphite and sodium bromid. The amounts present in the sulphite varied from 2 to 7 parts per million.

Minute Quantities of Chlorids in Chemical Reagents.[a]

(Determined by comparison of the silver chlorid opalescences.)

During the course of the examination of large numbers of chemicals in the drug laboratory of the Bureau of Chemistry it has been noticed that the ordinary qualitative test for chlorids indicates the presence of this impurity in a majority of the samples examined. It therefore appeared desirable to make a more careful study of the matter and if possible to discover the source of this frequent occurrence of chlorids in

[a] By L. F. Kebler and A. Seidell.

chemicals, and also to form an opinion regarding the establishment of an allowable limit for chlorids in various classes of chemicals.

The method employed for making the tests is briefly as follows: Aqueous solutions of weighed amounts of the chemicals to be tested are placed in 50 cc Nessler tubes, acidified with nitric acid, and aqueous silver nitrate solution added. The silver chlorid opalescences which result are compared with those developed in a similar manner in a series of Nessler tubes containing known amounts of a standard thousandth-normal hydrochloric acid solution. The comparisons were made in a room lighted by artificial light, observing the tubes from the side by means of reflected light.

The use of a nephelometer as described by Richards and Wells [a] would, undoubtedly, have permitted very much better readings, but unfortunately such an instrument was not at hand. The results obtained, however, are reasonably satisfactory for the purpose in view and are accurate to within 3 to 10 parts per million, depending upon the amount of sample used for making the test. In addition the method employed is one which can be used in any laboratory supplied with Nessler or large glass tubes.

Before beginning the actual examination of the samples of chemicals a number of experiments were made to ascertain to what extent the salts necessarily in the solution when the test is applied affect the intensity of the silver chlorid opalescence. It is stated by Wells [b] that concentrations of other salts in amounts less than 0.01 normal do not interfere with the production of the opalescence. This, however, applies to readings made with the very sensitive nephelometer and is no doubt a much smaller amount of salt than would seriously affect the accuracy of the comparison made according to the method used in the present work.

Since all tests are made in solutions acidified with nitric acid, the effect of this acid upon the opalescence was first determined. This was done by adding gradually increasing amounts of the purest nitric acid, which showed no chlorids when treated with silver nitrate, to 50 cc Nessler tubes and diluting to the mark with water; 1 cc portions of thousandth-normal hydrochloric acid were added to each tube and then 1 cc of 10 per cent silver nitrate solution. The opalescences produced were so nearly the same in all the tubes that no differences could be detected by the eye. The addition of 0.5 cc of thousandth-normal hydrochloric acid to some of the tubes produced differences which were easily distinguishable. It therefore appears that 60 parts by volume of concentrated nitric acid in 100 parts by volume does not appreciably affect the silver chlorid opalescences.

The presence of various amounts of sodium nitrate was next studied by adding gradually increasing amounts of concentrated sodium hydroxid solution (the sodium hydroxid being prepared from sodium and showing no chlorid when tested with silver nitrate) to the Nessler tubes and acidifying each solution with the pure nitric acid. One cubic centimeter of the thousandth-normal hydrochloric acid and one of the aqueous silver nitrate solution were added as before and the resulting opalescences proved to be identical. In addition to this test, a series of Nessler tubes was prepared with a concentrated sodium nitrate solution made as above and increasing amounts of thousandth-normal hydrochloric acid solution. Another series was prepared with water and increasing amounts of thousandth-normal hydrochloric acid. When the silver nitrate solution was added to the tubes of these two series it was found that the opalescences produced in corresponding tubes were the same as nearly as the eye could judge. From this it appears that to make the standards for judging the unknown samples it is equally as satisfactory to use water alone as to use concentrated chlorid-free solutions of the same salt that is under examination. Therefore, the standard tubes which were used in judging the amounts of chlorid in the samples enumerated in the following tables were made by adding known amounts of the standard thousandth-normal hydrochloric acid solution (1 cc, 2 cc, 4 cc, etc.) to Nessler tubes containing distilled water acidified with

[a] Amer. Chem. J., 1904, *31:* 235. [b] Amer. Chem. J., 1906, *35:* 99.

a few cubic centimeters of pure nitric acid and simultaneously treating these tubes, and the tubes containing the weighed amounts of the sample in solution, with the silver nitrate solution under similar conditions of light, temperature, etc.

The weight of sample ordinarily used was 10 to 20 grams, which was thoroughly shaken with 100 cc of water and 25 cc of the clear solution placed in the Nessler tubes and acidified with chlorid-free nitric acid. The opalescence was produced in all cases by the addition of 1 cc of 10 per cent silver nitrate solution.

It is to be regretted that the samples available in the laboratory at the time the examination was made were not representative of a larger number of manufacturers. There is reason to believe, however, that they exhibit the average quality of chemical reagents usually found in the market at the present day.

Among the first lot of chemicals examined for chlorids were the various salts of potassium, and the results which were obtained are given in Table 1.

The abbreviations used in the tables are as follows:

Mallinckrodt	Mallinckrodt Chemical Works, St. Louis, Mo.
B. and C	Bullock & Crenshaw, Philadelphia, Pa.
B. and A	Baker & Adamson Chemical Company, Easton, Pa.
Merck	Merck & Co., Darmstadt.
E. and A	Eimer & Amend, New York.
A. H. Thomas	A. H. Thomas Company, Philadelphia, Pa.
Schering	Germany.
Geo. D. Feidt	Philadelphia, Pa.
Kahlbaum	Germany.
B. and L	Bausch & Lomb Company, Rochester, N. Y.
Baker	J. T. Baker & Co.
Mackall Bros	Washington, D. C.
Henry Heil	St. Louis, Mo.

TABLE 1.—*Chlorids in potassium salts.*

Serial No.	Salt.	Description on label.	Source.	Parts per million.	
				Potassium chlorid.	Chlorin.
	Acetate	C. P. crystals	Mallinckrodt	None.	None.
491	do	do	do	None.	None.
833	do	do	B. and C	None.	None.
1341	do	do	B. and A	30	14
	Carbonate	do	Imported by E. and A	None.	None.
214	do		Merck	88	42
712	do	C. P. crystals	Imported by E. and A	59	28
821	do	do	B. and A	None.	None.
924	do	do	do	None.	None.
928	do	Reagent	Merck	59	28
1433	do	C. P. crystals	B. and A	None.	None.
	do	do	do	None.	None.
	Bicarbonate	do	Imported by E. and A	None.	None.
	do	do	do	147	70
249	do	Crystals, pure	Merck	None.	None.
511	do	C. P. crystals	Mallinckrodt	None.	None.
790	do		Diamond Soda Works	None.	None.
860	Citrate	Chemically pure	B. and A	30	14
968	do		E. and A	726	345
1173	do	Chemically pure	A. H. Thomas	30	14
215	Chromate	Yellow	Merck	360	171
325	do	Chemically pure	Mallinckrodt	None.	None.
425	do	do	do	None.	None.
573	do	do	do	None.	None.
1294	do	do	B. and A	120	56
1427	do	do	do	240	112
	do	do	do	60	28
211	Bichromate	Crystals, H. P	Merck	None.	None.
1282	do	Chemically pure	B. and A	60	28
1295	do	do	do	60	28
296	do	do	do	240	112
1441	do	do	do	30	14
1484	do	do	do	90	42
1000	do	do	do	90	42
	do	do	do	180	84
596	Hydroxid	Pure lumps	Schering	330	157
813	do	Pure by alcohol	B. and A	224	106

TABLE 1.—*Chlorids in potassium salts*—Continued

Serial No.	Salt.	Description on label.	Source.	Parts per million.	
				Potassium chlorid.	Chlorin.
225	Nitrate	Reagent	Merck	None.	None.
226	do	Highest purity	do	Trace.	Trace.
339	do	Chemically pure	Mallinckrodt	30	14
732	do	do	B. and C	30	14
669	do	do	Mallinckrodt	None.	None.
595	do	do	do	None.	None.
449	Nitrite	Sticks, C. P	E. and A	1,130	537
609	do	do	B. and A	4,520	2,130
230	Sulphate	Crystals, reagent	Merck	None.	None.
	do	Chemically pure	Geo. D. Feidt	59	28
895	do	do	B. and A	42	21
250	Bisulphate	Crystals, reagent	Merck	None.	None.
403	do	Chemically pure	Mallinckrodt	Trace.	Trace.
912	do	do	Geo. D. Feidt	Trace.	Trace.
1293	do	do	B. and A	6	3

TABLE 2.—*Chlorids in sodium salts.*

Serial No.	Salt.	Description on label.	Source.	Parts per million.	
				Sodium chlorid.	Chlorin.
268	Acetate	Chemically pure	B. and A	None.	None.
614	do	do	do	None.	None.
1174	do		Kahlbaum	None.	None.
1326	do	Chemically pure, crystals	B. and L	Trace.	Trace.
892	Biborate	Chemically pure	B. and A	Trace.	Trace.
1289	Tetraborate	Chemically pure, medicinal and toilet use.	Pacific Coast Borax Co	187	113
1317	do	do	do	70	42
232	Bicarbonate	Crystals, reagent	Merck	23	14
233	do	Powdered, H. P	do	46	28
623	do	Chemically pure	Mallinckrodt	None.	None.
633	do	do	B. and A	140	85
235	Carbonate	Anhydrous, H. P	Merck	46	28
236	do	Dried, reagent	do	None.	None.
301	do	Crystals, reagent	do	None.	None.
510	do	Anhydrous, C. P	B. and A	None.	None.
514	do	do	Mallinckrodt	46	28
570	do	Anhydrous, H. P	Merck	92	56
655	do	Anhydrous, C. P	B. and A	None.	None.
828	do	do	do	70	42
895	do	Anhydrous, H. P	Merck	46	28
956	do	Anhydrous, reagent	do	None.	None.
1048	do	Anhydrous, C. P	B. and L	140	84
1128	do	do	do	326	198
1135	do	do	A. H. Thomas	326	198
1142	do	Crystals, C. P	do	46	28
1146	do	do	do	46	28
1172	Citrate	U. S. P	do	70	42
239	Hydroxid	Purified reagent	Merck	2,340	1,418
240	do	Pure reagent	do	56	34
391	do	Pure by alcohol	Mallinckrodt	174	106
458	do	do	Merck	67	41
459	do	Pure reagent	do	71	43
473	do	Pure by alcohol	Mallinckrodt	77	47
551	do	Purified sticks	Merck	6,143	3,723
1419	do	Pure by alcohol	B. and A	203	123
1424	do	do	do	211	128
	do	Pure from sodium	Merck	None.	None.
242	Nitrate	Reagent	do	None.	None.
484	do	Chemically pure	Mallinckrodt	None.	None.
619	do	do	do	None.	None.
692	do	do	B. and A	117	71
610	Nitrite	do	do	47	28
871	do	do	do	None.	None.
1189	Peroxid		Roessler & Hasslacher	280	170
1227	do		do	163	99
1383	do	Free from S. P. and Cl	B. and L	47	28
244	Phosphate	Dried twice, purified	Merck	23	14
266	do	Chemically pure	Mallinckrodt	None.	None.
409	do	do	do	None.	None.
842	do	do	B. and A	23	14
1049	do	do	B. and L	70	42

TABLE 2.—*Chlorids in sodium salts*—Continued.

Serial No.	Salt.	Description.	Source.	Parts per million.	
				Sodium chlorid.	Chlorin.
1308	Phosphate	Chemically pure	B. and A	23	14
874	Salicylate	Crystals, H. P	Merck	None.	None.
234	Bisulphate	Reagent	do	12	7
305	do	Pure, dry reagent	do	None.	None.
1327	do	Chemically pure	B. and L	None.	None.
1431	do	do	do	None.	None.
267	Sulphate	do	Mallinckrodt	23	14
506	do	do	do	12	7
507	do	do	do	12	7
552	do	do	do	2,925	1,772
680	do	do	B. and A	70	42
944	do	do	Geo. D. Feidt	23	14
1046	do	do	B. and L	70	42
1212	do	do	do	70	42
	do	do	do	None.	None.
429	Sulphite	Crystals	Mackall Bros	70	42
1444	do	do	A. H. Thomas	47	28
	do	Chemically pure, dry	B. and A	140	84
413	Hyposulphite	Chemically pure	do	47	28
841	do	do	B. and C	93	54
1305	do	do	B. and A	117	70
690	do	do	B. and C	47	28
1400	Na and K tartrate	Rochelle salt, C. P	Mallinckrodt	None.	None.

TABLE 3.—*Chlorids in ammonium salts.*

Serial No.	Salt.	Description on label.	Source.	Parts per million.	
				Ammonium chlorid.	Chlorid.
865	Acetate	Chemically pure	B. and A	4½	3
1606	do	do	Baker	15	10
189	Carbonate	Reagent	Merck	10	7
832	do	Chemically pure	B. and A	None.	None.
	do	do	do	None.	None.
194	Nitrate	Crystals	Merck	15	10
195	do	Crystals, reagent	do	42	28
397	do	Chemically pure	Mallinckrodt	None.	None.
562	do	do	do	None.	None.
1123	do	do	B. and L	None.	None.
1342	do	do	do	4½	3
196	Oxalate	Reagent	Merck	None.	None.
931	do	Chemically pure	B. and A	21	14
	do	do	do	None.	None.
1134	do	do	B. and L	21	14
1500	do	do	do	30	21
814	Nitrate	do	B. and A	21	14
678	do	do	do	30	21
	do	do	do	21	14
197	Phosphate	Reagent	Merck	52	35
624	NH_4 and Na phosphate.	Chemically pure	Mallinckrodt	21	14
198	Sulphate	Reagent	Merck	4½	3
513	do	Chemically pure	Mallinckrodt	21	14
621	do	do	do	378	252
664	do	do	do	None.	None.
665	do	do	B. and A	4½	3
829	do	do	do	4½	3
	do	do	do	4½	3
401	Iron alum	do	Mallinckrodt	30	21

TABLE 4.—*Chlorids in calcium salts.*

Serial No.	Salt.	Description on label.	Source.	Parts per million.	
				Calcium chlorid.	Chlorid.
	Carbonate	Chemically pure	B. and A	10	7
651	do	do	do	10	7
825	do	do	do	66	42
575	Oxid	do	do	42	28
611	do	do	do	112	71
1122	do	do	do	31	21
	do	do	do	31	21
	do	do	do	10	7
431	Phosphate	Diabasic, reagent	Merck	10	7
636	do	Monobasic, G. R	do	21	14
1319	do	Diabasic, reagent	do	None.	None.
1387	do	Chemically pure	Baker	112	71
823	Sulphate	do	B. and A	31	21
897	do	do	Mallinckrodt	1,118	711
1508	do	do	B. and L	88	56

TABLE 5.—*Chlorids in barium salts.*

Serial No.	Salt.	Description on label.	Source.	Parts per million.	
				Barium chlorid.	Chlorin.
974	Acetate		Kahlbaum	63	21
703	Carbonate	Chemically pure	B. and A	42	14
866	do	do	do	21	7
1090	do	do	do	21	7
1116	do	do	do	21	7
1450	do	do	do	Trace.	Trace.
328	Hydroxid	do	Henry Heil	126	42
462	do	do	do	84	28
612	do	do	B. and A	63	21
947	do	do	A. H. Thomas	42	14
1449	do	do	B. and A	42	14
201	Nitrate	Powder	Merck	336	112
471	do	Chemically pure	B. and A	None.	None.
1083	do	do	do	42	14
1117	do	do	do	21	7
1425	do	do	do	21	7

TABLE 6.—*Chlorids in magnesium salts.*

Serial No.	Salt.	Description on label.	Source.	Parts per million.	
				Magnesium chlorid.	Chlorid.
1525	Oxid	S. free	B. and L	375	280
583	do	Chemically pure	B. and A	959	710
942	do	S. free	A. H. Thomas	141	105
558	Nitrate	Chemically pure	Mallinckrodt	9	7
482	Sulphate	do	B. and A	28	21
488	do	do	do	19	14

The results given in Table 1 indicate that the occurrence of objectionable amounts of chlorids in potassium salts is rather the exception, since nearly half of the samples examined contained no chlorids or only traces. Of the other samples it is seen that the chromate, nitrate, and hydroxid are the only ones in which the occurrence of excessive amounts of chlorids appears to be the rule. The acetate and bisulphate samples examined were found to be particularly free from this impurity. Of the other samples the amounts found are quite variable, and no conclusion in regard to the source of the chlorids present can be drawn.

The results included in Table 2 show that the acetate samples are practically free from chlorids. The borax samples are supposed to be of ordinary commercial quality,

and the amounts of chlorids found are no larger than might be expected. The bicarbonate and carbonate samples are quite variable, but it is seen that many of the samples are apparently free from chlorids, and therefore its elimination from material claimed to be chemically pure is evidently only a matter of care and experience on the part of the manufacturer. Passing over the one sample of citrate, it is seen that all the samples of hydroxid, with the single exception of the material made from metallic sodium, contain amounts of chlorids which vary over very wide limits. It therefore appears that in all samples of sodium hydroxid, except that made from the metal, the occurrence of chlorids is to be expected, and an allowable limit of this impurity in the best quality of goods should be fixed. From the results obtained it would appear that not exceeding 40 parts of chlorid per million should be a safe limit to adopt. The samples of nitrate, and also of nitrite, are apparently low in chlorids. The samples of peroxid, however, which are in fact sold as chlorid free, contain amounts which are appreciable, although probably not beyond the limits which would interfere with the use of the material for the determinations in which it is employed. The samples of phosphates examined show small amounts of chlorids, and it appears that such material can readily be purchased chlorid free. Although the bisulphite samples show small amounts or no chlorids, the samples of sulphates, sulphites, and hyposulphites are found to contain small amounts very generally distributed. One sample of sodium sulphite, for some unaccountable reason, is very high in the amount of this impurity.

The ammonium salts as exhibited in Table 3 are on the whole but slightly contaminated with chlorids. The amounts found, except, perhaps, in one case of ammonium sulphite, are too small to materially affect the quality of the samples.

The calcium and barium salts practically all show small amounts of chlorids, and its absolute elimination would probably require more effort than the advantage gained would repay.

In the case of magnesium oxid the presence of excessive amounts of chlorids is of general occurrence. In the nitrates and sulphates the amount present, however, is very much less.

The observations in the tables are only of general applicability. The results are mainly useful in indicating the general occurrence of chlorids in the chemicals at present found on the market.

The report on tannin having been referred to Committee B on recommendations of referees, after their adjournment Mr. Kebler offered a supplementary report on behalf of the committee to the effect that the work on tannin be continued by the association, and said recommendation was adopted.

The PRESIDENT. We have with us a visitor distinguished in this country and abroad, and I am sure that those who have not met him will be very glad to do so. I am going to call on Doctor de 'Sigmond, professor of agricultural chemistry in the University of Budapest, to address the association.

Doctor de 'Sigmond spoke in part as follows:

ADDRESS BY DR. ALEXIUS DE 'SIGMOND.

Mr. PRESIDENT AND GENTLEMEN OF THE ASSOCIATION: I am glad to have an opportunity of speaking to you of the excellent work of this convention. Especially in natural sciences—and agricultural chemistry is one of the main divisions of applied science—cooperation is much needed. In my researches I have found that while we may be sure of the exactness of our experimental results, we can not always be sure of the correctness of the conclusions drawn therefrom, and by cooperation we are able to

strengthen the weak parts of our conclusions by comparing our final results. This scientific cooperation should not only be national, but international, and I think I can perhaps contribute something to your work from mine.

I was particularly impressed by the address of the president of the association, and the line of work discussed by Doctor Hopkins is one with which I am very familiar, being in some ways similar to the work of Liebig, in Germany. In fact, the conditions in this country in some respects are similar to those in Hungary. The cornfields in Illinois and the wheat lands of the Northwest are like sections of our country where corn and wheat are the main crops. The same problem discussed by Doctor Hopkins, in regard to the proper manuring system, arises, and to prove whether the yield will decrease without fertilization more than 500 farm experiments were conducted, and in 70 per cent of these the phosphoric acid not only produced an effect, but proved profitable. The question, however, arose as to whether the farm experiments were conclusive, inasmuch as in several cases the results of the work were vitiated by conditions which could not be controlled. In order to provide a more accurate method of determining the need of fertilization, the experiment station of plant industry at Mazyar-Ovár, of which I was until lately the chemist, inaugurated about ten years ago the so-called Wagner experiments. These we found generally satisfactory, but great care was necessary, and considerable time—at least a season—inasmuch as we found evidence that different results were obtained during the first stages of growth and at the time of harvest. As the farmer wants these results more quickly, we turned to the chemical laboratory for a solution. We all know that the chemical methods for the determination of available plant food in the soil are not satisfactory; that is, they do not always agree with the results obtained in practice. This question I studied for five or six years, and my results may add something to your cooperative work.

The first question was to determine the most suitable solvent for the determination of available phosphoric acid. Schlösing found that if he treated a soil with pure water and gradually increased the amount of nitric acid in the water the quantity of phosphoric acid dissolved rapidly increased until a level was reached at which the increase ceased. The points at which these changes take place vary widely in different soils. Above these limits the amount of phosphoric acid dissolved again increases rapidly. This indicates to me that there is a difference between the natural solubilities of the phosphates in the soil which divides the phosphoric acid present into the soluble and the less soluble. I studied twelve different soils which all corroborated this idea.

The next point was to find out whether there is any relation between the quantity of slightly soluble phosphoric acid present and the amount needed in the soil. Experiments were made with 100 different soils analyzed by my method and tested both by field and pot experiments, and I was able to figure out in this way the practical limits of the phosphoric acid needed in the soils. At the same time I found that the reaction of the soil must be taken into consideration in drawing conclusions from the experimental results. For example, when an almost neutral soil needed phosphate, the slightly soluble phosphoric acid present never exceeded 0.007 to 0.015 per cent. On the other hand, in soils on which the phosphates produced practically no effect there was at least 0.075 per cent or more of soluble phosphoric acid present. This maximum limit was corroborated in all cases, but for the minimum limit—that is, the one showing the need of phosphoric acid in the soil—further classification was necessary. For example, in several cases soils rich in calcium carbonate and containing almost 0.050 per cent of soluble phosphoric acid still showed in the fertilizing experiments the need of phosphates. According to the experimental results, I was obliged, therefore, to classify the soils according to their basicity, it being the general rule that the increase of basicity of the soil decreases the availability of the soluble phosphates.

We also made extensive studies of our alkali soils, and it was gratifying to me when in California to find that the results obtained by Professor Hilgard are in close relation to those which I have found for such soils. I might state here that I have also used

with satisfaction some of the practical surveying methods of the Bureau of Soils of the United States Department of Agriculture.

Another question studied, which is not new but needs further attention, is the need of special fertilizers by different plants. We have found, for instance, that wheat needs a great deal of available phosphoric acid in the early period of its development, while corn can take it later; therefore, when we fertilize corn, a phosphate of lower availability can be used than for wheat, because the corn can utilize a less available form.

I will not pursue this discussion further, but will conclude my remarks with a cordial invitation to each member of this association to come to our country and investigate our experimental fields and work; you will find us investigating problems very similar to your own.

After some discussion the following motion was passed as to the place of meeting for the convention of 1907:

Resolved, That the place of meeting in 1907 be left to the discretion of the executive committee, the preference of the association being understood to be for Norfolk, if deemed practicable, when the call for the meeting is issued.

Mr. Veitch. Last year the referee submitted a revised method for the determination of tannin. The committee on revision of methods has made some changes, chiefly in manner of statement, etc., in this method, and I move that the method as revised by the committee be substituted as the provisional method of the association.

The motion was carried.

REPORT ON POTASH.

By A. L. Knisely, *Referee*.

The work this year has been devoted to the determination of potash in one sample of soil and in one sample of mixed fertilizer containing considerable organic matter. Upon the sample of soil the official and the proposed volumetric methods were used; upon the sample of fertilizer the official methods for water soluble and for total potash (K_2O) were used; also the proposed ignition method, the proposed volumetric method, and Carpenter's method.

The directions sent to the cooperating chemists were as follows:

Association Potash Work.

Sample No. 1.—A typical soil from the wheat-growing belt of Sherman County, Oreg. Ninety-nine and seven-tenths per cent of this soil passes readily through a 0.5 mm sieve. This soil contains, approximately, 1.50 per cent of total potash (J. Lawrence Smith method) and from 0.25 to 0.5 per cent acid soluble potash.

Sample No. 2.—A mixed fertilizer containing considerable nitrogen, phosphoric acid, and potash—approximately 7 to 9 per cent of potash (K_2O).

association work upon soil.

Mix thoroughly before sampling.

1. Determine potash (K_2O) in soil according to official method using hydrochloric acid 1.115 sp. gr. (Bul. 46, revised, p. 71).
2. Proposed volumetric method for potash in soils.

Reagents.

Nitric acid—5.5 cc nitric acid, 1.40 sp. gr., in 1,000 cc water.

Sodium nitrate wash—5 grams sodium nitrate per 1,000 cc water.

Phosphomolybdic solution—100 grams phosphomolybdic acid (Kahlbaum's preferred) in 750 cc water and 250 cc nitric acid 1.40 sp. gr.

Standard solutions—Standard caustic potash and nitric acid prepared for volumetric phosphoric acid. One cc of potassium hydroxid is equal to 1.655 mg of potash (K_2O).

Determination.

Take a fresh aliquot portion, representing 1 gram, of solution A under soil analysis (Bul. 46, revised, p. 72) in a porcelain dish, add 10 cc phosphomolybdic solution and evaporate to dryness. Add 25 cc nitric acid wash heated to 50° C., and stir thoroughly. Allow to cool, filter through a thick asbestos filter, and wash with sodium nitrate wash until free from acid; transfer the gooch to a tall beaker, add an excess of standard potassium hydroxid and heat nearly to boiling (any precipitate adhering to the crucible should be dissolved with the standard alkali). When the precipitate is completely dissolved add a few drops of phenolphthalein, which should show an excess of alkali, and titrate back with standard nitric acid.

ASSOCIATION WORK UPON MIXED FERTILIZER.

Mix thoroughly before sampling.

1. In sample No. 2 determine water soluble potash (K_2O) according to the official method (Bul. 46 revised, p. 21).

2. In sample No. 2 determine total potash (K_2O) in organic compounds by the official method (Bul. 46, revised, p. 22, (*b*) *With organic compounds*).

3. *Proposed method.*—Ignite 5 grams of sample No. 2 at dull redness to a gray ash. Transfer to 200 cc beaker, using 25 cc of hot approximately 10 per cent hydrochloric acid to remove last traces, cover with watch glass and let simmer on hot plate for one-half hour; then add 100 cc water and to hot solution add slight excess ammonia and ammonium oxalate, cool, make up to 250, filter through dry filter. Evaporate 50 cc of filtrate and proceed as under 3 (*a*) in mixed fertilizers (Bul. 46, revised, p. 22).

4. *Proposed volumetric method.*—Ignite 5 grams of sample No. 2 at dull redness to a gray ash. Transfer to 200 cc beaker, using 25 cc of hot approximately 10 per cent hydrochloric acid to remove last traces, cover with watch glass and let simmer on hot plate for one-half hour, cool, make up to 250 cc, filter through dry filter, take 25 cc of filtrate in a porcelain dish, add 20 cc phosphomolybdic solution, and evaporate to dryness; add 50 cc nitric acid wash heated to 50° C. and stir thoroughly. Proceed as under proposed volumetric method for potash in soils.

5. *Carpenter's proposed method.*—Boil 10 grams of the sample with 300 cc of water plus 5 cc of hydrochloric acid for thirty minutes. Add a few drops of phenolphthalein and carefully neutralize with sodium hydrate free from potash, avoiding a large excess. Add sufficient powdered ammonium oxalate to precipitate all the lime present, cool, dilute to 500 cc, mix and pass through a dry filter. Complete determination by official method (Bul. 46, p. 22).

In each case run blanks to ascertain corrections to be made for impurities. (It is necessary to ascertain blank in phosphomolybdic solution.) It is also advisable to treat the potassium platinic chlorid residue in the gooch crucible in order to ascertain if it is all soluble in water. Then reweigh the crucible after thoroughly drying.

If any workers have time, it is suggested that they make a determination of potash in each of the two samples according to a method suggested by F. P. Veitch (J. Amer. Chem. Soc., January, 1905, pp. 56–61).

A. L. Knisely, *Referee.*
B. B. Ross, *Associate Referee.*

Comparison of official and modified methods for the determination of potash in soil and in mixed fertilizer.

Analyst.	Soil.		Fertilizer.				
	Official.	Volumetric.	Official water-soluble.	Official total.	Proposed ignition method.	Proposed volumetric.	Carpenter's method.
Stillwell and Gladding, New York City	*Per cent.*	*Per cent.*	*Per cent.* 8.50	*Per cent.*	*Per cent.* 9.40	*Per cent.*	*Per cent.* 9.00
W. D. Richardson, Swift & Co., Chicago	0.47	0.48	8.77	8.93	8.76	8.57	8.98
	.47		8.71	8.80	8.81	8.62	9.00
			8.64			8.74	8.96
R. W. Thatcher, Washington station	.40	[a].38	8.76	[c]7.95	8.95	[c]7.96	[c]7.99
	.39	[b].40	8.77	[c]7.97	8.98	[c]7.99	[c]7.89
		[a].41	8.71		8.85		
		[b].40					
W. E. Dickinson, South Carolina station	.47	.45					
	.45	.47					
B. F. Robertson, South Carolina station	.47	.51	8.73	8.85	8.83	8.79	
J. H. Mitchell, South Carolina station	.47		8.73	8.74	8.81	8.69	
L. Heimburger, Agricultural Department, Tallahassee, Fla.	.41	.40	9.04	9.13	8.73	9.08	8.92
	.41	.43	9.00	9.05	8.74	9.12	
		.39				9.14	
						8.98	
						8.95	
F. A. Welton, Ohio station	.48		8.82		8.89		8.82
M. G. Donk, Bureau of Chemistry, Washington, D. C.	.45	.45	8.67	8.84	9.09	9.45	9.25
	.47	.41	8.72		8.84	9.60	9.04
		.46				9.27	
C. E. Bradley and A. L. Knisely, Oregon station	.41	.39	8.49	8.82	8.17	8.73	8.89
	.42	.41	8.49	8.83	8.24	8.82	8.99
	.42	.40	8.50		8.36		
	.41						
	.44						
Average	.439	.426	8.71	8.89	8.78	8.97	8.98
Maximum	.48	.51	9.04	9.13	9.40	9.60	9.25
Minimum	.39	.38	8.49	8.74	8.17	8.57	8.82
Difference	.09	.13	.55	.39	1.23	1.03	.43

[a] Without evaporating to dehydrate silica.
[b] After evaporating to dehydrate silica.
[c] Omitted from average.

Since the foregoing results vary considerably, the question may be raised as to the proper sampling of the fertilizer. Samples were prepared as follows:

The mixed fertilizer was finely ground and sifted upon a large piece of flexible oilcloth. The sample was thoroughly mixed by rolling alternate corners of the oilcloth. After thorough mixing, about 10 grams of the sample were placed in each of 40 sample bottles, the fertilizer remaining on the oilcloth was again thoroughly mixed and a second 10 grams put in each sample bottle. This process of mixing and sampling was continued until all the fertilizer was used.

The contents of each sample bottle of fertilizer was mixed by shaking and rolling, after which the contents of all sample bottles were again emptied on the oilcloth and thoroughly remixed. The sample bottles were again filled in the manner previously described and immediately sealed with paraffin.

Comments by Analysts.

Thomas S. Gladding: The results obtained are interesting and seem to show that the method by ignition and solution in acid is the only method that gives total available potash present.

R. W. Thatcher: The volumetric method seems to me to be very promising. I find difficulty in getting anything like a satisfactory sample of phosphomolybdic acid from any of our American dealers, and think that it will be practically necessary for each analyst to prepare his own material for use in this method.

W. E. Dickinson: It seems to me that the volumetric method is too greatly affected by varying conditions to be used successfully by beginners.

L. Heimburger: In the volumetric method, with both samples No. 1 and No. 2, the best results were obtained with smaller samples than recommended, due probably to the difficulty encountered in washing the potassium phosphomolybdate free from all the excess of phosphomolybdic acid.

F. A. Welton: Concordant results were not obtained by the volumetric method on either sample.

M. G. Donk: I was unable to get concordant results using 0.5 gram of material, as directed, as the precipitate on using this quantity of material was of such a coherent nature that it was not possible to wash it entirely free of the excess of reagents used. The results reported were obtained by using 0.1 gram of material, 5 cc of phosphomolybdic solution, and 20 cc of nitric acid wash.

Comments by Referee.

Nitric acid heated to 50 ° C. exerts a marked solvent action on the potassium phosphomolybdate. This is especially marked in soil work where potash is present in small amount. For this reason cold nitric acid saturated with pure potassium phosphomolybdate was used instead. The acid solution of the soil was directly evaporated with the phosphomolybdic acid, as results by this method agreed closely with those made on solution A, Bulletin 46, page 72.

No difficulty was experienced in making results on the fertilizer by the official method agree when made on the same solution; but different solutions of the same sample, supposed to be made in identically the same way, gave results that in some cases varied considerably.

The method of ignition and subsequent solution in acid gives slightly higher results than the official method for water soluble potash. The referee does not believe that this extra potash should be placed on the same basis with the water soluble.

Additional Results.

Some additional results, received too late to be included in the averages, are given in the following table:

Additional potash determinations made on referee's samples.

Analyst.	Soil.	Fertilizer.			
	Official method.	Official water soluble method.	Proposed ignition method.	Proposed volumetric method.	Corpenter's proposed method.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
G. S. Fraps, Texas station	0.63	9.01 9.06 9.02		8.99 8.98	8.90 8.96 8.97
F. G. Keyes, Rhode Island station			8.88 8.76 9.12		
W. F. Purrington, Rhode Island station			8.99 9.03 9.04	9.03 9.05 9.05	

Mr. Hartwell writes as follows in regard to the work reported from the Rhode Island station:

In the case of the gravimetric method, Mr. Keyes took 5 grams of the sample and made it up to 250 cc, taking only 25 cc for each determination, whereas Mr. Purrington made the solutions in a similar manner, but took 50 cc for each determination, or the equal of a half gram of the sample, as is required by the official method.

The blank determination with the gravimetric method was equal to 3 mg of potassium chlorplatinate, and this blank has been deducted from each analyst's results before reporting the percentages. In the case of the volumetric method, the blank was equal to 0.2 cc of the standard potassium hydroxid solution. This blank has likewise been deducted before reporting the results, and in all cases a correction was made for calibration of the glassware. In the case of the gravimetric results, the factor 0.194[a] was used to convert the potassium chlorplatinate to potassium oxid.

RECOMMENDATION.

The referee recommends a continuation of the study of the volumetric method for use in both soil and fertilizer analysis.

Mr. CUSHMAN. It seems to me that the association should consider this important question of potash determination in another way. The work consists now in a comparison of methods for the determination of total and water-soluble potash, but should we not determine whether there is any potash present and available that is not water soluble? It is possible to put a definite weight of potassium chlorid into an acid-phosphate fertilizer and then have the official analysis show less potash than was added. Again, it is possible to make up a solution of potassium chlorid, and after it has been shaken with a natural clay some of the potash disappears from the solution into the clay, but it is not possible to wash the clay and regain the potash. The point I am making is that the method of leaching with water does not tell the truth, for the potash held by absorption in the clay would be available as plant food. Again, in a wet feldspar powder three kinds of potash must be recognized—that in the crystalline compound which has not yet been set free, that set free but held by absorption in the decomposed product, and that which goes freely into solution in water. Is it true, then, as so many chemists believe to-day, that only one of these three kinds of potash is available as plant food? My belief is that two of these are available, the water soluble and that held by absorption in the colloidal decomposition products of the material. I have extracted from a feldspar containing 9 per cent of total potash 3 per cent, using only water, but that same sample referred to a commercial chemist and analyzed by the official method was returned as containing only 0.1 per cent of available potash. I maintain that our methods are unsatisfactory as long as such a condition is possible. If I can extract from a finely-ground feldspar by the use of distilled water a large part of the potash present, it is possible that the same thing takes place in nature, and there is no evidence to show that by leaching a finely-ground material with water all of the potash available as plant food is obtained. On the other hand, there is abundance of evidence to show that there is more potash present available as plant food that does not go into water solution under the conditions

[a] This factor is given by König in Die Untersuchung landwirtshaftlich und gewerblich wichtiger Stoffe, 1906, p. 30.

of our present analytical process. In view of these facts, I wish to recommend that the referee direct his attention to a study of what really constitutes available potash in soils, fertilizers, and ground mineral products, so that, if possible, we may have a definition of available potash. The referee, I understand, according to the precedents and rules of our association, has the right to call in subreferees, or at least other members of the association, to aid him in making his report. If there were any machinery for doing it, I think the matter so important that I would suggest the appointment of a representative committee to study the question carefully, but as it is I recommend that the referee turn his attention to a definition of available potash.

Mr. Hartwell. It seems to me that Mr. Cushman is laboring under a misapprehension as to the attitude of the association. Hardly any one experienced in soil work would claim that the water-soluble potash necessarily represented the available potash in a given fertilizer. We have, however, in many of the States, laws which distinctly state that potash shall be determined as water soluble. This is not saying that it represents the available potash; in fact, if we are using the plant, the only true measure of the availability, as the standard, the availability will vary with the plant used. What, then, shall be considered as available potash? That which is available to the turnip or to some other crop? These questions are well recognized by the members of the association and will, I think, be considered in future work. Perhaps it might be well for the referee to conduct pot experiments for the purpose of determining this question.

Mr. Frear. The purpose of analyzing fertilizers is primarily to determine to what extent they contribute plant food to the soil, and while the general principles are fairly well understood they are subject to change as the work progresses. I think we have all been deeply interested in the results of Mr. Cushman's work with minerals which are ordinarily supposed not to give up their basic substances within any short interval. But the problem which confronts the chemist is this: Here is one class of materials conceded to contain immediately available plant food and another class which contains the same ingredients but in a form much less quickly available if at all so. The temptation is to resort to the use of the latter class, at the same time guaranteeing the same high percentage of nutrient constituents. While critical studies along this line are in place, I think the work of the chemist must for some time continue to consist in the distinction between materials of high and low value.

Mr. Bowker. I do not think that there is a fertilizer manufacturer of any repute who desires to introduce into his goods insoluble forms of potash, for if the analytical tests were not satisfactory, the results

in the field would not be, and after all the final test is the field test. Do they give satisfaction to the farmer? We are using large quantities of cotton-seed meal and other legitimate substances which contain organic forms of potash. Under the present methods of examination no credit is given for that potash, and I think the methods ought to be changed to correct this. When we make an acid phosphate and add to it muriate of potash, about 10 per cent of phosphoric acid and 8 per cent of potash, there is, for some unaccountable reason, a loss of from 5 to 10 per cent of the potash present according to the official returns. I ask this association, as the officials who stand between us and the consumer, if that is fair? It is true the laws say that water-soluble potash shall be determined, but those laws are based, I think, on the Massachusetts law, which was framed back in 1873, before we had experiment stations, when the idea was that only water-soluble materials were available. The original laws called for water-soluble phosphoric acid, but to-day reverted phosphoric acid is recognized and determined by an arbitrary method. I maintain that if it is right to recognize two forms of phosphoric acid there should be methods for determining two forms of potash. We may ask for an amendment to the law in Massachusetts this year which will provide for such determinations, and I think our experiment station will work with us. In my opinion Mr. Cushman is doing a great work. Every year we pay enormous sums to Germany for imported potash, but the experiments performed by Mr. Cushman before the chemists in Boston in obtaining potash from finely ground rock by electrolysis open up the possibility of obtaining our potash from the feldspar deposits in this country.

Mr. Cushman's motion was referred to committee A for action.

REPORT OF COMMITTEE A ON RECOMMENDATIONS OF REFEREES.

By R. J. Davidson, *Chairman*.

(1) Nitrogen.

It is recommended:

1. That the work on the Fuller modification of the official Gunning method be discontinued, and that the Gunning method remain as it is now stated.

Adopted.

2. (a) That the work on the neutral permanganate method be continued along the same lines as this year, having in mind the influence of excessive amounts of nonnitrogenous material in the source of nitrogen. (b) That work be directed along the line of eliminating some of the many details of the method which influence to too great a degree the results obtained.

Adopted.

3. That the work on the alkaline permanganate method be continued and that the quantity of material taken be changed to 0.0675 gram nitrogen; that the quantity of alkaline permanganate used in digestion be changed to 150 cc, and that 100 cc be distilled off before titration. The modified method should read as given on page 83.

Referred to the referee for 1907 for investigation as to whether this method or some

modification of it can be applied to all organic nitrogenous materials, especially cotton-seed meal.

4. That the method for standardizing hydrochloric acid proposed in 1905 and referred to the referee for 1906 be adopted and that the method now given in the official methods be dropped. [See Bul. 46, Rev., p. 14, under "4. Determination of nitrogen." The proposed method reads as follows:

By means of a preliminary test with silver-nitrate solution, to be measured from a burette, with excess of calcium carbonate to neutralize free acid and potassium chromate as indicator, determine exactly the amount of nitrate required to precipitate all the hydrochloric acid. To a measured and also weighed portion of the standard acid add from a burette one drop more of silver-nitrate solution than is required to precipitate the hydrochloric acid. Heat to boiling, cover from the light, and allow to stand until the precipitate is granular. Then wash with hot water through a Gooch crucible, testing the filtrate to prove excess of silver nitrate. Dry the silver chlorid at 140° to 150° C.

Adopted as the official method.

[Note by the secretary.—The following method for the estimation of nitrogen was submitted by Mr. T. S. Gladding, together with comparative results on 81 samples obtained by the three methods compared, the question being raised as to whether a combination of two official methods, the Gunning and the Kjeldahl, would be considered an official method. Mr. Gladding requested that appropriate action be taken, and the method is submitted for the information of the referee without instructions from the association:

COMBINATION METHOD: KJELDAHL AND GUNNING METHODS.

One gram of fertilizer; 25 cc of sulphuric acid; 10 grams of potassium sulphate; 0.7 gram of mercuric oxid; heat till water white. Cool, add 200 cc of water, 0.5 gram of zinc dust, 25 cc of potassium sulphid solution, 50 cc of soda solution, and distil.]

(2) Separation of Nitrogenous Bodies.

A. MILK AND CHEESE PROTEIDS.

It is recommended:

1. That the original method of preparing the water extract [cheese analysis], proposed by Van Slyke and Hart, be so altered as to call for the use of 1,000 cc of water in place of 500 cc. [Proceedings, 1902, Bul. 73, p. 89.]

Adopted.

2. That the method of drawing the water extract through a thick pad of asbestos, after it has been separated from the fat and insoluble nitrogenous matter by cotton wool, be further studied.

Adopted.

3. That the temperature at which the extraction is made be further studied.

Adopted.

4. That the completeness of the extraction of matter soluble in salt solution be further studied.

Adopted.

B. VEGETABLE PROTEIDS.

The report of the referee was received too late for action to be taken by committee A, but the following recommendation is submitted as a matter of record:

It is recommended, for the purpose of securing greater uniformity of results, that in the extraction of alcohol-soluble nitrogen in wheat and flour 70 per cent alcohol by weight, sp. gr. 0.871, be used.

C. MEAT PROTEIDS.

It is recommended:

1. That the modified tannin-salt method as described in the proceedings of the association for 1905 [Bureau of Chemistry Bul. No. 99, p. 182] be adopted as a provisional method.

Referred again to the referee for recommendation in 1907.

2. That the xanthin base method of Schittenhelm [Proceedings, 1904, Chemistry Bul. No. 90, p. 129] be adopted as a provisional method.

Referred again to the referee for recommendation in 1907.

3. That the application of the kreatinin method as applied by Folin to the urine be further studied by the association. [Zts. physiol. Chem., 1886, *10:* 391.]

Adopted.

(3) INORGANIC PLANT CONSTITUENTS.

It is recommended:

That the peroxid method for total sulphur be adopted as official.

[This method was recommended as provisional by the referee in 1905, Bul. No. 99, p. 133, the restatement of the method given on page 152 varying only in technique.]

Referred to referee for 1907 for recommendation as to final action.

2. That the combustion method (i. e., the Sauer-Tollens-Barlow method) for determining volatile inorganic plant constituents be further investigated. [Sauer, Zts. anal. Chem., 1873, *12:* 32; Barlow-Tollens, J. Amer. Chem. Soc., 1904, *26:* 341.]

(4) POTASH.

It is recommended:

1. That the study of the volumetric method for use in both soil and fertilizer analysis be continued. [Proceedings, 1905, Bureau of Chemistry, Bul. No. 99, p. 135.]

Adopted.

2. The following recommendation, made by Mr. Cushman, was referred to committee A after their report had been made. The committee, however, considered the recommendation subsequent to the adjournment and referred it to the referee on potash for investigation.

I recommend that the referee direct his attention to a study of what really constitutes available potash in soils, fertilizers, and ground-mineral products, so that, if possible, we may have a definition of available potash. The referee, I understand, according to the precedents and rules of our association, has the right to call in subreferees, or at least other members of the association, to aid him in making his report. If there were any machinery for doing it in the association, I think the matter so important that I would suggest the appointment of a representative committee to study the question carefully; but as it is I put it in the form of a recommendation, that the referee turn his attention to a definition of available potash.

(5) SOILS.

It is recommended:

1. That the fifth-normal nitric-acid digestion method be further studied. [Bul. No. 46, p. 74 (i), using nitric instead of hydrochloric acid and digesting at 20° C. instead of 40° C.]

Adopted.

2. That the sodium-peroxid fusion method for total phosphorus be given a further trial, and that this be compared with the alkali-carbonate fusion method. [Proceedings, 1905, Bul. 99, p. 111; details slightly modified in 1906 report.]

Adopted.

3. That the modified J. Lawrence Smith method for total potassium, presented at this meeting (p. 147), be further tested.

Adopted.

4. That line 30, under "1. Preparation of sample," page 71, Bulletin No. 46, be changed from "openings ½ millimeter in diameter," to "openings 1 millimeter in diameter," and that "passed through a sieve of 1-millimeter mesh" be omitted from line 1 under "(h), page 74."

This change in an official method, having been before the association in 1905, was adopted.

5. That for "3. Determination of volatile matter," Bulletin No. 46, page 72, substitute the Determination of Total Organic Carbon [J. Amer. Chem. Soc., 1904, *26:* 1640] as the official method.

Recommended for adoption as official in 1907.

6. That under (k), page 75, Bulletin No. 46, mark the official method "(a)" and insert the following:

B. OPTIONAL PROVISIONAL METHOD.

Proceed as in (a) through "let stand a few minutes in the water bath" and complete as follows:

Filter into a beaker, add a drop or two of hydrochloric acid and 1 cc of ammonium sulphate (75 grams to 1 liter), digest several hours on water bath, and filter into a tared platinum dish. Evaporate to *complete* dryness, heat to dull redness, add 1 gram of powdered ammonium carbonate, expel by heating, cool, and weigh the sulphates of sodium and potassium. Determine potassium in the usual manner.

Adopted.

(6) INSECTICIDES.

It is recommended that the methods submitted for investigation in 1905 be further studied. These methods are as follows:

1. Work on London purple, special attention being given to the modifications proposed by Mr. Davidson for the removal of part of the color.

DAVIDSON'S MODIFICATION.

Total arsenious oxid.

Place 2 grams of London purple in a beaker and dissolve in about 80 cc of water and 20 cc of concentrated hydrochloric acid at a temperature of 80°. Cool and add sodium carbonate in slight excess, transfer to a 250 cc flask, and bring to the mark; shake and filter through a dry filter into a dry beaker; acidify 50 cc with hydrochloric acid and add sodium bicarbonate, titrating with iodin as usual.

Total arsenic oxid.

Acidify 50 cc of the alkaline solution, prepared as described under "Total arsenious oxid," with hydrochloric acid, add 25 cc of concentrated hydrochloric acid and 3 grams of potassium iodid. Then proceed as directed under this determination in Circular 10, revised, Bureau of Chemistry, page 4.

2. The hydrogen peroxid method for determining sulphur in sulphur dips and similar compounds, effort being made to have all analyses made simultaneously.

3. The hydrogen peroxid method for determining formaldehyde in its modified form.

4. The methods of determining available chlorin in bleaching powder.

Motion carried.

REPORT OF COMMITTEE ON THE PRESIDENT'S ADDRESS.

The committee appointed to consider the President's address begs leave to submit the following report:

(1) In view of the general interest of the subject under discussion to others than agricultural chemists we recommend that a special edition of the president's address be published separately from the Proceedings for wide distribution.

(2) Inasmuch as there is not sufficient time during this convention to give the matter the full consideration which it deserves, we recommend that a committee be appointed which shall, after consultation with the Secretary of Agriculture, consider in detail the questions raised in the address and report at the next meeting of the association.

F. W. Woll.
L. L. Van Slyke.
A. L. Winton.[a]
B. B. Ross.
R. J. Davidson.
A. M. Peter.
C. L. Penny.

The report of the committee was adopted by the association.

REPORT OF COMMITTEE ON UNIFICATION OF TERMS FOR REPORTING ANALYTICAL RESULTS.

Mr. R. J. Davidson, as chairman of this committee, reported certain recommendations to the association, stating, however, that only meager responses had been received from the chemists consulted during the two years that the matter had been under consideration, during which time two preliminary reports had been submitted in circular form for criticism. In the discussion which followed, participated in by Messrs. Frear, Davidson, Penny, Bigelow, and Hopkins, it appeared that the association was not ready to vote on the recommendations, and that a wider expression of opinion was desirable, especially from the American Chemical Society and the agricultural colleges and experiment stations, before taking any definite action. Mr. Davidson again called attention to the fact that every endeavor had been made to obtain an expression of the views of chemists at large with but slight response, and the committee was rather at a loss as to how to proceed further in the matter. After some further discussion, especially as to the merits of the element system of nomenclature, it was ordered that action on the report be deferred until another year and the committee continued.

REPORT OF THE COMMITTEE ON RESOLUTIONS.

By L. L. Van Slyke.

Resolved, That we extend to the Secretary of Agriculture and the Assistant Secretary of Agriculture our hearty thanks for the continued assistance which they have so generously given to this association.

Resolved, That we acknowledge the courtesies of the George Washington University and thank it for the use of these rooms for our convention.

Resolved, That the secretary convey to the Cosmos Club an expression of the hearty appreciation of the members of this association for the courtesies extended to them by the club.

The report of the committee was adopted and the association adjourned.

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[a] Mr. Winton later resigned, and the vacancy was filled by the appointment of Mr. J. G. Lipman.

OFFICERS, REFEREES, AND COMMITTEES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR THE YEAR 1907.

President.

Mr. JOHN P. STREET, New Haven, Conn.

Vice-President.

Mr. HARRY SNYDER, St. Anthony Park, Minn.

Secretary.

Mr. H. W. WILEY, Washington, D. C.

Additional members of Executive Committee.

Mr. B. B. Ross, Auburn, Ala.
Mr. B. L. HARTWELL, Kingston, R. I.

Referees.

Phosphoric acid: B. W. Kilgore, Raleigh, N. C.
Nitrogen:
Determination of nitrogen: C. L. Penny, Newark, Del.
Separation of nitrogenous bodies: L. L. Van Slyke, Geneva, N. Y. (milk and cheese proteids).
Potash: A. L. Knisely, Corvallis, Oreg.
Soils: J. H. Pettit, Urbana, Ill.
Dairy products: F. W. Woll, Madison, Wis.
Foods and feeding stuffs: J. K. Haywood, Washington, D. C.
Food adulteration: A. E. Leach, Boston, Mass.
Sugar: C. A. Browne, jr., Washington, D. C. (Special analytical methods.)
Tannin: F. P. Veitch, Washington, D. C.
Insecticides: R. J. Davidson, Blacksburg, Va.
Inorganic plant constituents: W. W. Skinner, Washington, D. C.
Medicinal plants and drugs: L. F. Kebler, Washington, D. C.

Associate referees.

Phosphoric acid: J. M. McCandless, Atlanta, Ga.
Nitrogen:
Determination of nitrogen: G. W. Cavanaugh, Ithaca, N. Y.
Separation of nitrogenous bodies—
Meat proteids: F. C. Cook, Washington, D. C.
Vegetable proteids: Harry Snyder, St. Paul, Minn.
Potash: B. B. Ross, Auburn, Ala.
Soils: S. D. Averitt, Lexington, Ky.
Dairy products: J. M. Bartlett, Orono, Me.
Foods and feeding stuffs: John P. Street, New Haven, Conn.

Food adulteration:

(1) Colors: E. F. Ladd, Agricultural College, N. Dak.
(2) Saccharine products, including confectionery: C. H. Jones, Burlington, Vt.
(3) Fruit products: H. C. Lythgoe, Boston, Mass.
(4) Wine: Julius Hortvet, St. Paul, Minn.
(5) Beer: H. E. Barnard, Indianapolis, Ind. (General associate on food adulteration.)
(6) Distilled liquors: L. M. Tolman, Washington, D. C.
(7) Vinegar: Charles H. Hickey, Boston, Mass.
(8) Flavoring extracts: E. M. Chace, Washington, D. C.
(9) Spices: A. L. Winton, Chicago, Ill.
(10) Baking powder and baking chemicals: W. M. Allen, Raleigh, N. C.
(11) Meat and fish: E. L. Redfern, Lincoln, Nebr.
(12) Fats and oils: L. M. Tolman, Washington, D. C.
(13) Dairy products: A. E. Leach, Boston, Mass.
(14) Cereal products: A. McGill, Ottawa, Canada.
(15) Vegetables: W. L. Dubois, Washington, D. C.
(16) Condiments other than spices: R. E. Doolittle, New York.
(17) Cocoa and cocoa products: E. M. Bailey, New Haven, Conn.
(18) Tea and coffee: C. D. Howard, Concord, N. H.
(19) Preservatives: W. D. Bigelow, Washington, D. C.
(20) Determination of water in foods: F. C. Weber, Washington, D. C.

Sugar:

Molasses methods: J. E. Halligan, Baton Rouge, La.
Chemical methods: Fritz Zirban, Audubon Park, La.

Tannin: M. S. McDowell, State College, Pa.

Insecticides: F. S. Shiver, Clemson College, S. C.

Inorganic plant constituents: John W. Ames, Wooster, Ohio.

Medicinal plants and drugs: Charles H. La Wall, Philadelphia, Pa.

SPECIAL COMMITTEES.

Food Standards.

Mr. William Frear, State College, Pa., chairman.
Mr. H. W. Wiley, Washington, D. C.
Mr. H. A. Weber, Columbus, Ohio.
Mr. M. A. Scovell, Lexington, Ky.
Mr. E. H. Jenkins, New Haven, Conn.

Fertilizer Legislation.

Mr. H. W. Wiley, Washington, D. C., chairman.
Mr. B. W. Kilgore, Raleigh, N. C.
Mr. H. B. McDonnell, College Park, Md.
Mr. J. L. Hills, Burlington, Vt.
Mr. B. B. Ross, Auburn, Ala.

Testing Chemical Reagents.

Mr. L. F. Kebler, Washington, D. C., chairman.
Mr. A. L. Winton, Chicago, Ill.
Mr. B. W. Kilgore, Raleigh, N. C.

Unification of Terms for Reporting Analytical Results.

Mr. R. J. Davidson, Blacksburg, Va., chairman.
Mr. C. G. Hopkins, Urbana, Ill.
Mr. W. D. Bigelow, Washington, D. C.
Mr. G. S. Fraps, College Station, Tex.
Mr. C. A. Browne, jr., Washington, D. C.

Committee on the President's Address.

Mr. F. W. Woll, Madison, Wis., chairman.
Mr. R. J. Davidson, Blacksburg, Va.
Mr. C. L. Penny, Newark, Del.
Mr. A. M. Peter, Lexington, Ky.
Mr. B. B. Ross, Auburn, Ala.
Mr. L. L. Van Slyke, Geneva, N. Y.
Mr. J. G. Lipman, New Brunswick, N. J.

Committee on Revision of Methods.

Mr. J. K. Haywood, Washington, D. C., chairman.
Mr. F. P. Veitch, Washington, D. C.
Mr. L. M. Tolman, Washington, D. C.
Mr. J. P. Street, New Haven, Conn.
Mr. A. L. Winton, Chicago, Ill.
Mr. J. H. Pettit, Urbana, Ill.
Mr. F. W. Woll, Madison, Wis.

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) This association shall be known as the Association of Official Agricultural Chemists of the United States. The objects of the association shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statement of analysis of fertilizers, soils, cattle foods, dairy products, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State or national agricultural experiment station or agricultural college, or with any State or national institution or body charged with official control of the materials named in section 1, shall alone be eligible to membership; and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to enter motions or vote in the association. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers. All persons eligible to membership shall become members ex officio and shall be allowed the privileges of membership at any meeting of the association after presenting proper credentials. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members and to have all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall not be entitled to enter motions or vote.

(3) The officers of the association shall consist of a president, a vice-president, and a secretary, who shall also act as treasurer; and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee, to continue in office till the annual meeting next following.

(4) There shall be appointed by the executive committee, at the regular annual meeting, a referee and such associate referees for each of the subjects to be considered by the association as that committee may deem appropriate.

It shall be the duty of these referees to prepare and distribute samples and standard reagents to members of the association and others desiring the same, to furnish blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

(7) No changes shall be made in the methods of analysis used in official inspection, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of the particular inspection affected to test the proposed changes.

(8) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(9) The executive committee will confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(10) All proposed alternations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by the approval of two-thirds of the members present entitled to vote.

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